

ANALYSIS OF NATURAL GAS BY FT-IR; CALIBRATIONS & VALIDATIONS

**INTERIM REPORT
TFLRF No. 324**

By
G.E. Fodor
U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI)
Southwest Research Institute
San Antonio, Texas

Under Contract to
U.S. Army TARDEC
Mobility Technology Center-Belvoir
Fort Belvoir, Virginia

Contract No. DAAK70-92-C-0059

Approved for public release; distribution unlimited

May 1997

[DTIC QUALITY INSPECTED 3]

19970512 092

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Trade names cited in this report do not constitute an official endorsement or approval of the use of such commercial hardware or software.

DTIC Availability Notice

Qualified requestors may obtain copies of this report from the Defense Technical Information Center, Attn: DTIC-OCC, 8725 John J. Kingman Road, Suite 0944, Fort Belvoir, Virginia 22060-6218.

Disposition Instructions

Destroy this report when no longer needed. Do not return it to the originator.

| REPORT DOCUMENTATION PAGE | | | Form Approved OMB No. 0704-0188 | |
|--|---|--|---|--|
| Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instruction, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503. | | | | |
| 1. AGENCY USE ONLY (Leave blank) | | 2. REPORT DATE May 1997 | 3. REPORT TYPE AND DATES COVERED Interim November 1994 to February 1997 | |
| 4. TITLE AND SUBTITLE Analysis of Natural Gas by Fourier Transform Infrared Spectroscopy – Calibrations & Validations | | | 5. FUNDING NUMBERS DAAK70-92-C-0059; WD 37 | |
| 6. AUTHOR(S) Fodor, George E. | | | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI) Southwest Research Institute P.O. Drawer 28510 San Antonio, Texas 78228-0510 | | | 8. PERFORMING ORGANIZATION REPORT NUMBER TFLRF No. 324 | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Army Mobility Technology Center-Belvoir 10115 Gridley Road, Suite 128 Ft. Belvoir, Virginia 22060-5843 | | | 10. SPONSORING/MONITORING AGENCY REPORT NUMBER | |
| 11. SUPPLEMENTARY NOTES | | | | |
| 12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited | | | 12b. DISTRIBUTION CODE | |
| 13. ABSTRACT (Maximum 200 words) A fast experimental protocol was established for the simultaneous determination of methane, ethane, propane, and butane in nitrogen from Fourier transform infrared (FT-IR) spectra. The method is based on correlations established between known gas compositions and their FT-IR spectra. The spectra were collected in the region of 4,000 to 400 cm ⁻¹ through KBr windows in a 100-mm pathlength gas sample cell operating at 100, 300, 500, 700, and 1,000 mm Hg pressure. Correlation between blending partial pressure or GC-based analysis and FT-IR data produced squared correlation coefficients (R ²) in excess of 0.98. Total required analytical time is less than 2 minutes. | | | | |
| 14. SUBJECT TERMS Natural gas Analysis Infrared spectroscopy FT-IR | | | 15. NUMBER OF PAGES 50 | |
| | | | 16. PRICE CODE | |
| 17. SECURITY CLASSIFICATION OF REPORT Unclassified | 18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified | 19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified | 20. LIMITATION OF ABSTRACT | |

EXECUTIVE SUMMARY

Problem: Traditionally, natural gas has been analyzed by relatively cumbersome and time-consuming gas chromatographic methods that are not conveniently adaptable to field use.

Objective: The objective of this program was to investigate and define the use of midband Fourier transform infrared (FT-IR) spectroscopy as a rapid and reliable means of estimating natural gas composition and derived properties in the field.

Importance of Project: This method provides a quick and simple way of estimating the concentrations of the major natural gas components and their derived properties simultaneously. Compared to the gas chromatographic procedure, the spectroscopic method offers advantages in cost, time required per analysis, and adaptability to use in remote locations.

Technical Approach: Since methane, ethane, propane, and butane each have distinct infrared spectra, the measurement of their individual concentration can be performed. Using standards, calibration models were constructed to correlate actual concentration of components with FT-IR spectra. The calibration models were validated using a set of independently procured and analyzed natural gas samples.

Accomplishments: A fast experimental protocol was established for the simultaneous determination of methane, ethane, propane, and butane in nitrogen using FT-IR spectroscopy. The spectra were collected in the region of 4,000 - 400 cm^{-1} wavenumbers in a 100 mm pathlength gas sample cell at absolute pressures between 100 and 1,000 mm Hg. Correlation between blending partial pressure, or GC-based analysis, and FT-IR data produced squared correlation coefficients (R^2) in excess of 0.98. Limited validation experiments indicate that FT-IR spectra, taken at 500 mm Hg absolute sample cell pressure provides favorable analysis for the $\text{C}_1 - \text{C}_4$ natural gas components down to one mole percent concentration. Computer output of compositional data may also include values for various composition related properties, *e.g.*, heat of combustion, carbon-to-hydrogen ratio, and density. Using commercially available equipment, these analyses may be performed in the laboratory or in the field.

Military Impact: Improved analytical chemical speed and convenience facilitates obtaining compositional data on natural gas in the laboratory or in the field. The method may also be adopted as an on-line analyzer for natural gas pipelines.

DTIC QUALITY INSPECTED 3

FOREWORD/ACKNOWLEDGMENTS

This work was performed by the U.S. Army TARDEC Fuels and Lubricants Research Facility (TFLRF) located at Southwest Research Institute (SwRI), San Antonio, Texas, during the period November 1994 to February 1997 under Contract No. DAAK70-92-C-0059. The work was funded by the U.S. Army Tank-Automotive Research, Development and Engineering Center (TARDEC), Warren, Michigan. Mr. T.C. Bowen (AMSTA-RBFF) of Mobility Technology Center-Belvoir (MTCB) served as the contracting officer's representative and technical monitor.

This report is a continuation of Interim Report TFLRF No. 319, entitled "Analysis of Natural Gas by Fourier Transform Infrared Spectroscopy," in which results of only the calibration experiments were included. The current report includes the development of both the calibration models and the validation of these models.

The author would like to acknowledge the support provided by S.J. Lestz, E.C. Owens, E.A. Frame, R.L. Mason, S.A. Hutzler and K.H. Childress. Laboratory assistance provided by M.S. Voigt and J.J. Dozier is gratefully appreciated. Also acknowledged is the support provided by K.M. Kelley, and W.C. Mills.

TABLE OF CONTENTS

| <u>Section</u> | <u>Page</u> |
|----------------------------------|-------------|
| I. INTRODUCTION | 1 |
| II. OBJECTIVE | 2 |
| III. APPROACH | 2 |
| IV. EXPERIMENTAL | 3 |
| V. CHEMOMETRICS | 4 |
| VI. RESULTS AND DISCUSSION | 6 |
| A. Calibrations | 6 |
| B. Validations | 8 |
| VII. CONCLUSIONS | 10 |
| VIII. REFERENCES | 10 |
| APPENDICES | |
| A. Tables | 13 |
| B. Figures | 23 |

LIST OF ILLUSTRATIONS

| <u>Figure</u> | <u>Page</u> |
|--|-------------|
| 1 Schematic diagram of gas sampling system | 4 |

I. INTRODUCTION

Composition of natural gas in pipelines is not constant.¹ King demonstrated that, as expected, the composition of natural gas will have a marked effect on the operational characteristics of engines burning natural gas as the fuel.² Kubesh and coworkers showed that gas composition has a significant effect on the octane number of natural gas blends used as fuel in internal combustion engines.³ For these reasons and for determining values in product custody transfers, a reliable, quick, and accurate method was needed to determine gas composition that is more convenient and timely to perform than the commonly used gas chromatographic method.

Between 85 and 95 volume percent (vol%) of pipeline quality natural gas is methane. Generally, the balance of the gas is ethane, propane, butane, and inert gases. Although some studies have found measurable amounts of higher molecular weight hydrocarbons, it was shown that the components present in natural gas at concentrations of less than 0.2 mole percent (mol%) do not contribute significantly to the calorific value of the natural gas.⁴ For this reason, a natural gas may be adequately described by the concentrations of the four lightest saturated hydrocarbons, i.e., methane through butane. From the concentrations of the major active ingredients, several pertinent gas properties, e.g., heating value, density, etc., may be easily calculated by built-in computers.

FT-IR and near-IR spectroscopies have the potential to meet the requirements of an on-line or a transportable natural gas analyzer. Near-infrared (near-IR) spectroscopy generally operates in the 900 to 2,000 nanometer (nm), or 0.9 to 2.0 micrometer (μm), wavelength region. Midband Fourier transform infrared (FT-IR) spectroscopy is normally used in the 2.0 to 50 μm region. Due to limitations of optical window materials, FT-IR is usually used in the restricted spectral region from about 2.5 to 25 μm , corresponding to 4,000 to 400 cm^{-1} wavenumbers. In comparing near-IR with FT-IR, it may be noted that near-IR is the result of second and third overtones and combination bands of the fundamental frequencies that produce the directly measurable FT-IR region of the infrared spectrum. Since FT-IR spectroscopy is based on the measurement of characteristic fundamental resonances, it produces specific, usually sharp, well-defined peaks at

substantially increased extinction coefficients. Potentially, these facts lead to higher analytical specificity, accuracy, and sensitivity. The higher sensitivity manifested by FT-IR allows accurate measurement of the various natural gas components at substantially reduced pressures.

Brown and Lo demonstrated the feasibility of near-IR in monitoring the energy content of natural gas.⁵ The quartz optics and fiber-optic probes typically used with near-IR instruments allow the analyzer to be positioned remote to the measurement site, making it adaptable to field use.⁶ Westbrook⁷ used near-IR to analyze natural gas at 207 kPa (30 psig) in a flowing line. During the FT-IR analysis of gasolines and turbine and diesel fuels, Fodor et al. demonstrated that the use of infrared spectroscopic analyses, combined with multivariate calibration techniques, allowed the estimation of several pertinent fuel properties. In these experiments the accuracy of measurements was comparable to measurements from techniques that were designed to directly measure the desired fuel properties.⁸⁻¹⁰

II. OBJECTIVE

The objective of this program was to explore the use of midband FT-IR spectroscopy as a rapid and reliable laboratory or field method to estimate natural gas composition and derived properties and to demonstrate the feasibility of FT-IR as an on-line natural gas analyzer.

III. APPROACH

Reference or calibration gases were blended according to compositions determined by statistical treatment of the natural gas compositional limits to maximize the expected correlational output using a minimum number of samples. FT-IR spectra were generated from each of these quantitatively blended reference gas mixtures. The same blends were also analyzed by gas chromatography (GC) to substantiate their composition. Using these data, calibration models were developed for methane, ethane, propane, and butane in nitrogen.

IV. EXPERIMENTAL

Compositions of calibration gas mixtures were designed using the E-CHIP statistical program. The experimental design included the four C_1 - C_4 saturated hydrocarbons in nitrogen to provide the minimum number of standard samples, allowing calibration within the widest expected concentration ranges for each component:

| | |
|----------|----------------|
| methane | 50 to 100 vol% |
| ethane | 0 to 10 vol% |
| propane | 0 to 30 vol% |
| butane | 0 to 5 vol% |
| nitrogen | 0 to 35 vol% |

To properly blend the various gas components, a four-port mixing manifold was fabricated, and regulating needle valves were installed at each port. Quantitative blending of calibration gas standards was performed using a precision vernier "pressure volume controller" and a pressure regulator and monitor (Heise Models PTE-1 and HBC-1000). A schematic diagram of this sampling system is shown in Fig. 1. The calculated compositional data on these calibration standard mixtures are given in TABLE A-1 of Appendix A. Concentrations of components of the calibration gas standards were confirmed by GC using an instrument (Hewlett-Packard Model 5890 Series II) equipped with a gas sampling valve and a thermal conductivity detector. A GC method, based on the procedure described in ASTM D 1945-91 (Standard Method for the Analysis of Natural Gas by Gas Chromatography), was used as the benchmark method for the analysis of all natural gas samples. Matheson Gas Co. primary standards were used to calibrate the GC. The operating conditions of the GC are summarized in TABLE A-2. To facilitate quantitative FT-IR analysis, pressure control was provided by the same precision pressure regulator that was used for the blending operations. Temperature control relied on the constant temperature environment of the spectrometer's internal sample compartment.

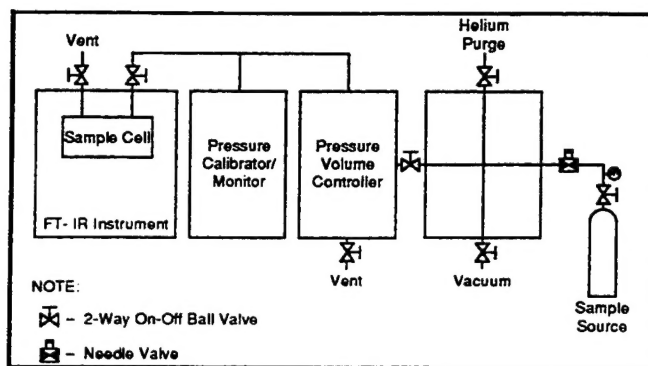


Figure 1. Schematic diagram of gas sampling system

The 100 mm pathlength gas cell was equipped with KBr windows. Spectra of the average of 32 FT-IR scans of each gas sample were collected on all 44 calibration gas mixtures at a resolution of 2 cm^{-1} within the $4,000$ to 400 cm^{-1} wavenumber spectral region at 100, 300, 500, 700, and 1,000 mm Hg absolute cell pressure. The various applied gas pressures served to optimize FT-IR response to the vastly different concentration ranges of the natural gas components.

V. CHEMOMETRICS

Spectroscopic data were correlated to fuel property values using Galactic Industries' PLSplus chemometric software package within the GRAMS/386 program. Since all gas components will exhibit only carbon-hydrogen bonds in their IR spectra, no regions were excluded from building the correlation models.

The PLS method creates a simplified representation of the spectroscopic data by a process known as spectral decomposition. Good summary treatises of PLS were published by Martens and Naes¹¹ and by Haaland and Thomas.^{12,13} The PLS approach is based on a bilinear modeling method. A precursor to the PLS technique, which is closely linked to the bilinear framework used in PLS, is the latent root regression analysis, formulated in the 1970's by Webster, Gunst, and Mason.¹⁴ The PLS algorithm initially calculates the concentration, or property value, weighted average

spectrum of all the spectra of the fuels in the calibration matrix. This calculation is followed by a computationally intensive procedure, accomplished by performing cross-validation calculations for all samples in the training set. In the cross-validation procedure, a given number of samples (in this study, two) are removed from the calibration data set, and a calibration model, calculated from the remaining samples in the training set, is used to predict the concentration (property value) of the removed samples. The residual errors, or the difference between the predicted and known concentration values, are squared and summed to determine the prediction error. Repeating this cross-validation process for the other samples in the training set results in a refined regression model that is useful in predicting the properties of unknown fuels. The results of spectral decomposition give one set of scores and one set of factors (loading vectors) for calibration for each component of interest. After a calibration model is established, it must be tested by validation experiments in which the calibration model is applied to similar fuels that were not part of the calibration training set. The predicted property values may then be compared with those derived by established ASTM procedures.

It is critical to establish the correct number of factors to be used in the correlation files, because the predicted fuel property values calculated from the model depend upon the number of factors used in the model. Too few factors will not adequately model the system, while too many factors will introduce noise vectors in the calibration, resulting in less than optimum prediction for samples outside the calibration set. The PLS program by Galactic Industries provides data for selecting the appropriate factor by plotting the prediction residual error sum of squares (PRESS) versus the factor. The factor may be selected for (a) the point at which the PRESS value is at a minimum, normally corresponding to a maximum in the value of the squared correlation coefficient, R^2 , (b) the point at which the curve indicates that further increase in factors should have negligible effects (a rather arbitrary choice), or (c) a compromise as recommended by Haaland and Thomas. These authors advise the use of an F -statistic to arrive at the best compromise in factors. The F -statistic can be calculated as the ratio of the minimum PRESS value to all PRESS values corresponding to fewer factors. As the difference between the minimum PRESS and other PRESS values become smaller, the probability, p , that each additional factor will provide significant improvement to the model becomes smaller. Haaland and Thomas

empirically determined that the optimum number of factors should be at the first PRESS value, where the F -statistic probability drops below 0.75. Initially, we used factors corresponding to an F -statistic probability of 0.5, coinciding with the maximum for the squared correlation coefficients. However, to avoid possible overfitting, we standardized by using the compromise value of $p \leq 0.75$, as suggested by Haaland and Thomas.

VI. RESULTS AND DISCUSSION

A. Calibrations

The synthetic blends of pure components were mixed following the E-CHIP statistical design guidelines. Concentrations of the individual components, expressed in mole percent (mol%), were available by calculation from the blending partial pressure data and the supporting GC data. The FT-IR spectra were collected at ambient temperature at gas sample cell absolute pressures of 100, 300, 500, 700, and 1,000 mm Hg.

The FT-IR spectra of the pure calibration gas components (methane, ethane, propane, butane, and nitrogen), obtained at absolute gas cell pressure of 100 mm Hg, are shown in Figs. B-1 through B-5 in Appendix B. Nitrogen has no active infrared resonance band.

The raw, unmodified spectroscopic data were correlated to both sets of concentration data (*i.e.*, those derived from blending partial pressures and those obtained from GC analysis) for methane, ethane, propane, butane, and the IR-inactive inert diluting nitrogen, using Galactec Industries' PLSplus chemometric software package. Since all gas components exhibit only carbon-hydrogen bonds in their IR spectra, no spectral regions were excluded from building the correlation models. To maintain simplicity of operation without adverse effects on measurement capabilities, no baseline segments were excluded from the calibration files.

Data derived from both the blending partial pressure information and from gas chromatographic data were used for the calibrations. A summary of the data from the pressure and GC-derived calibration experiments is summarized in TABLES A-3 and A-4, respectively. As expected, these

two data sets gave essentially identical results, therefore further illustrations show only the pressure-derived data.

Figures B-6 and B-7 in Appendix B are barcharts derived from TABLES A-3 and A-4 using the factors obtained at minimum PRESS and at $p \leq 0.75$, respectively. These figures show that R-squared values for all of the calibrations are above 0.95, and if the 700 mm Hg data for butane are excluded, all R-squared values are above 0.98.

The excellent agreement between the calibration standards and FT-IR derived concentration data is illustrated in Figs. B-8 through B-12 for methane, ethane, propane, butane, and nitrogen, respectively, using factors at the compromise $p \leq 0.75$. Further information is given in the bracketed area of each figure for (a) the number of factors, F , (b) the sum of the absolute value of the differences between the known and FT-IR derived concentrations for all the samples, or total error, TE, (c) squared correlation coefficient, R^2 , and (d) root mean squared difference, RMSD, an indication of the average error in the analysis. Figures B-13 through B-17 show the relationship between the standard error of cross-validation, SECV, and the sample cell pressures for the five components using factors corresponding to (a) minimum PRESS and (b) $p \leq 0.75$ values. In the case of methane (and the inert, inactive diluent nitrogen), the SECV decreases with increasing pressure while remaining fairly constant with the C_2 - C_4 hydrocarbons. This suggests that improved analytical data may be obtained for methane at elevated pressures. However, using a 100 mm gas cell at elevated pressures, all of these hydrocarbons displayed spectra with some peaks in the nonlinear range of the absorbance, indicating detector overload. For instance, such detector overload may be observed in case of methane for each of the two characteristic resonance bands, *i.e.*, at $3,014\text{ cm}^{-1}$ due to asymmetric stretching and at $1,303\text{ cm}^{-1}$, the result of asymmetric bending. Note, however, the reduced error (SECV) for methane at the higher calibration pressures (concentrations) in comparison with those of the other components.

As discussed earlier, to avoid problems caused by overfitting, it is desirable to use the smallest number of factors in the model that yields acceptable data. During our calibrations, we used up to 20 factors. Factors associated with minimum in PRESS values, or at $p \leq 0.75$, were lowest for

all five components at sample cell pressures of 100 mm Hg. These data are shown in Figs. B-18 and B-19.

It should be noted that computer output of measurement results may also show composition related properties, *i.e.*, properties that may be calculated from compositional data, *e.g.*, the heat of combustion, carbon-to-hydrogen ratio, density, etc. These are key properties used for air/fuel ratio management in engines, or for gas custody transfers.

B. Validations

Following the calibration studies on synthetic natural gas compositions, the method was validated by applying the developed calibration models to FT-IR spectra of independently obtained and analyzed natural gas samples.

Prior to comparing the GC and FT-IR derived data, experiments were carried out to establish the realistic precision of the benchmark GC method. A natural gas standard, prepared and analyzed by Scott Specialty Gas Co., was used to establish GC analytical repeatability. The Scott gas sample was analyzed by the GC method 15 times, and the sample standard deviation was calculated. TABLE A-5 provides a summary of the GC analyses, including the applicable ASTM repeatability values, the known concentration values, the average of the GC data, and a measure of error in the GC analysis. Results indicate that the average residual error, *i.e.*, the average of the arithmetic difference between the average GC data and the known data, is -0.13 mol% for methane, 0.02 mol% for ethane, and 0.01 mol% for propane and butane. When percent error is calculated, the resultant figures are 0.15, 0.57, 1.00, and 2.50 percent for methane through butane, respectively.

The FT-IR derived analytical results were evaluated by comparing them to the GC data. As practiced during the calibration experiments, an FT-IR spectrum was taken for each sample at

absolute pressures of 100, 300, 500, 700, and 1,000 mm Hg. Compositional analyses of these samples were derived from these spectra by using the appropriate calibration models.

Two methods were used to evaluate correlations between the GC and the FT-IR methods. A simple way of assessing the agreement between the benchmark and new measuring techniques considers the residual errors (arithmetic differences) between the established and new methods. Another procedure uses the "limits of agreement."¹⁵ This method is recommended in cases where the results of the benchmark method may be uncertain. To generate the limits of agreement between the generally accepted (GC) and new (FT-IR) methods, the residual error is plotted against the average value of the two methods, and the results are evaluated at one and two standard deviations, *e.g.*, Difference Value \pm 2 standard deviation (Difference Values).

Results of the validation experiments are given in TABLES A-6a and A-6b. In these tables the results of analysis for each of nine validation samples are presented for methane, ethane, propane, butane, and for the IR-inactive, diluent "nitrogen." The presented data include (a) the GC data, (b) the FT-IR derived data as measured at five pressures, and (c) the residual error. The residual error in the validation experiments are shown in Figure 20, and the sample standard deviation of the residual errors are shown in Figure 21. The limits of agreement data are provided in Figs. B-22 through B-26 for methane, ethane, propane, butane, and diluting, inert, IR-inactive "nitrogen."

It may be concluded that 500 mm Hg absolute sample cell pressure provides a good overall compromise to achieve favorable analysis for the C₁ - C₄ natural gas components down to one mole percent concentration using FT-IR spectroscopy.

VII. CONCLUSIONS

A fast experimental protocol was established for the simultaneous determination of methane, ethane, propane, and butane in nitrogen using FT-IR spectroscopy. The spectra were collected in the region of 4,000 – 400 cm^{-1} wavenumbers in a 100 mm pathlength gas sample cell at absolute pressures between 100 and 1,000 mm Hg. Correlation between blending partial pressure, or GC-based analysis, and FT-IR data produced squared correlation coefficients (R^2) in excess of 0.98.

Limited validation experiments indicate that FT-IR spectra, taken at 500 mm Hg absolute sample cell pressure provides favorable analysis for the C_1 – C_4 natural gas components down to one mole percent concentration. Computer output of compositional data may also include values for composition related properties, e.g., the heat of combustion, carbon-to-hydrogen ration, density.

VIII. REFERENCES

1. Liss, W.E. and Thrasher, W.H., "Natural Gas as a Stationary Engine and Vehicular Fuel," SAE Paper No. 912364, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, **1991**.
2. King, S.R., "The Impact of Natural Gas Composition on Fuel Metering and Engine Operational Characteristics," SAE Paper No. 920593, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, **1992**.
3. Kubesh, J., King, S.R., and Liss, W.E., "Effect of Gas Composition on Octane Number of Natural Gas Fuels," SAE Paper No. 922359, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, **1992**.
4. Skrbic, B.D. and Cvejanov, J.D., "Comparative Analysis of Methods for Determination of Calorific Values of Natural Gas Mixtures," *Fuel Processing Technology*, **1991**, 28, pp. 307-314.
5. Brown, C.W. and Lo, S-C., *Appl. Spec.*, **1993**, vol. 47, No. 6, pp. 812-815.
6. Westbrook, S.R., "Army Use of Near-Infrared Spectroscopy to Estimate Selected Properties of Compression Ignition Fuels," SAE Paper No. 930734, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, **1993**.

7. Westbrook, S.R., "The Feasibility of Using Near-Infrared Spectrometer to Estimate Selected Properties of Natural Gas," SAE Paper No. 940762, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, **1994**.
8. Fodor, G.E. and Kohl, K.B., "Analysis of Middle Distillate Fuels by Midband Infrared Spectroscopy," *Energy & Fuels*, **1993**, vol. 7, No. 5, pp. 598-601.
9. Fodor, G.E., "Analysis of Petroleum Fuels by Midband Infrared Spectroscopy," SAE Technical Paper No. 941019, Presented at the SAE 1994 International Congress & Exposition, Detroit, MI, February 28-March 3, **1994**.
10. Fodor, G.E., Kohl, K.B., and Mason, R.L., "Analysis of Gasolines by FT-IR Spectroscopy," *Analytical Chemistry*, **1996**, vol. 68, pp. 23-30.
11. Webster, J.T., Gunst, R.F., and Mason, R.L., *Technometrics*, **1974**, vol. 16, pp. 513-522.
12. Martens, H.A. and Naes, T., *Multivariate Calibration*, Wiley, New York, **1989**.
13. Haaland, D. and Thomas, E.V., *Analytical Chemistry*, **1988**, vol. 60, pp. 1193-1202.
14. Haaland, D. and Thomas, E.V., *Analytical Chemistry*, **1988**, vol. 60, pp. 1202-1208.
15. Bland, J.M. and Altman, D.G., *Statistician*, **1983**, vol. 32, pp. 307-317.

APPENDIX A

Tables

| | | |
|------|--|----|
| A-1 | Calibration Gas Mixture Composition (mol%) | 15 |
| A-2 | Gas Chromatographic Conditions | 16 |
| A-3 | FT-IR Calibration for Natural Gas Components (Based on Blending Partial Pressures of Synthetic Standards) | 17 |
| A-4 | FT-IR Calibration on Natural Gas Components (Based on GC Analysis of Synthetic Blend of Standards) | 18 |
| A-5 | GC Analysis of a Scott Natural Gas Standard | 19 |
| A-6a | Validation of Calibration Models for Natural Gas Components at 100 mm Hg, 300 mm HG, & 500 mm Hg | 20 |
| A-6b | Validation of Calibration Models for Natural Gas Components at 700 mm Hg & 1,000 mm Hg | 21 |

Table A-1. Calibration Gas Mixture Composition (mol%)

| <u>Methane</u> | <u>Ethane</u> | <u>Propane</u> | <u>Butane</u> | <u>Nitrogen</u> |
|----------------|---------------|----------------|---------------|-----------------|
| 61.13 | 2.77 | 1.42 | 0.00 | 34.68 |
| 100.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 74.66 | 0.00 | 0.00 | 0.00 | 25.34 |
| 63.88 | 0.00 | 21.69 | 0.00 | 14.50 |
| 61.13 | 9.97 | 3.61 | 0.00 | 25.29 |
| 49.98 | 10.65 | 0.00 | 5.02 | 34.36 |
| 54.86 | 10.17 | 0.00 | 0.00 | 34.97 |
| 86.58 | 0.00 | 8.30 | 5.11 | 0.00 |
| 49.60 | 9.90 | 8.23 | 3.63 | 28.64 |
| 75.10 | 11.58 | 8.37 | 4.95 | 0.00 |
| 49.04 | 0.00 | 25.97 | 3.91 | 21.08 |
| 82.99 | 7.31 | 0.00 | 0.00 | 9.71 |
| 89.98 | 10.02 | 0.00 | 0.00 | 0.00 |
| 49.87 | 2.92 | 30.04 | 0.00 | 17.18 |
| 59.19 | 6.25 | 12.60 | 5.00 | 16.96 |
| 49.96 | 9.77 | 22.97 | 0.00 | 17.30 |
| 57.69 | 9.47 | 28.11 | 4.73 | 0.00 |
| 100.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 53.57 | 5.03 | 3.77 | 2.55 | 35.90 |
| 49.73 | 0.00 | 15.18 | 0.00 | 35.08 |
| 96.26 | 0.00 | 0.00 | 3.74 | 0.00 |
| 86.21 | 10.12 | 0.00 | 3.66 | 0.00 |
| 49.84 | 7.32 | 12.09 | 0.00 | 30.75 |
| 69.70 | 0.00 | 30.30 | 0.00 | 0.00 |
| 53.70 | 0.00 | 30.12 | 1.41 | 14.76 |
| 71.31 | 0.00 | 0.00 | 3.61 | 25.08 |
| 49.67 | 0.00 | 30.40 | 5.10 | 14.96 |
| 49.80 | 0.00 | 10.03 | 5.10 | 35.07 |
| 86.13 | 0.00 | 8.44 | 0.00 | 5.43 |
| 92.19 | 2.76 | 0.00 | 5.06 | 0.00 |
| 75.12 | 0.00 | 0.00 | 0.00 | 24.88 |
| 63.87 | 5.02 | 14.02 | 0.00 | 17.08 |
| 68.10 | 10.36 | 21.54 | 0.00 | 0.00 |
| 85.03 | 0.00 | 0.00 | 5.09 | 9.87 |
| 59.79 | 0.00 | 0.00 | 5.25 | 34.96 |
| 52.84 | 10.01 | 29.94 | 0.00 | 7.21 |
| 77.50 | 4.74 | 15.25 | 2.52 | 0.00 |
| 66.11 | 0.00 | 29.07 | 4.82 | 0.00 |
| 66.83 | 3.01 | 0.00 | 4.99 | 25.16 |
| 49.67 | 10.25 | 0.00 | 5.07 | 35.01 |
| 54.72 | 10.06 | 30.21 | 5.02 | 0.00 |
| 74.38 | 10.14 | 0.00 | 4.97 | 10.52 |
| 63.14 | 10.16 | 0.00 | 1.39 | 25.30 |
| 49.87 | 7.24 | 29.81 | 3.66 | 9.42 |

TABLE A-2. Gas Chromatographic Conditions

| | | |
|---------------------------------|--|----------|
| Instrument: | Hewlett-Packard model 5890 Series II | |
| Detector: | Thermal conductivity, 250°C | |
| Injector: | Gas sampling valve, 0.25 mL sample loop, 125°C | |
| Column: | Porapak QS, 40/60 mesh, 4.6 m × 3.2 mm (15 ft × 1/8 in.) stainless steel packed column | |
| Carrier Gas: | Helium | |
| Flow Rates: | Analytical: 20 mL/min | |
| | Reference: 30 mL/min | |
| Column Program: | Initial temperature: | 100°C |
| | Initial hold: | 0 min |
| | Rate: | 20°C/min |
| | Final temperature: | 225°C |
| | Final hold: | 4 min |
| Total Analytical Time Required: | Approx. 15 min | |

**TABLE A-3. FT-IR Calibration for Natural Gas Components
Based on Blending Partial Pressures of Synthetic Standards**

| <u>Compound</u> | <u>P* (abs) mm Hg</u> | <u>at min. PRESS</u> | | | <u>at $p \leq 0.75$</u> | | |
|-----------------|---------------------------|----------------------|-------------|----------------------|------------------------------------|-------------|----------------------|
| | | <u>F</u> | <u>SECV</u> | <u>R²</u> | <u>F</u> | <u>SECV</u> | <u>R²</u> |
| methane | 100 | 4 | 1.652 | 0.9891 | 3 | 1.804 | 0.9872 |
| | 300 | 7 | 1.350 | 0.9928 | 6 | 1.410 | 0.9922 |
| | 500 | 11 | 1.184 | 0.9944 | 8 | 1.301 | 0.9932 |
| | 700 | 11 | 1.138 | 0.9948 | 8 | 1.234 | 0.9940 |
| | 1000 | 13 | 0.664 | 0.9982 | 11 | 0.714 | 0.9980 |
| ethane | 100 | 8 | 0.179 | 0.9985 | 7 | 0.198 | 0.9981 |
| | 300 | 9 | 0.254 | 0.9969 | 7 | 0.268 | 0.9966 |
| | 500 | 9 | 0.193 | 0.9982 | 8 | 0.214 | 0.9978 |
| | 700 | 12 | 0.200 | 0.9981 | 10 | 0.218 | 0.9977 |
| | 1000 | 20 | 0.138 | 0.9991 | 18 | 0.151 | 0.9989 |
| propane | 100 | 11 | 0.350 | 0.9992 | 5 | 0.365 | 0.9991 |
| | 300 | 20 | 0.479 | 0.9984 | 19 | 0.522 | 0.9981 |
| | 500 | 20 | 0.376 | 0.9990 | 17 | 0.414 | 0.9988 |
| | 700 | 18 | 0.650 | 0.9971 | 15 | 0.711 | 0.9965 |
| | 1000 | 20 | 0.469 | 0.9985 | 17 | 0.509 | 0.9982 |
| butane | 100 | 13 | 0.152 | 0.9956 | 11 | 0.158 | 0.9952 |
| | 300 | 18 | 0.223 | 0.9906 | 17 | 0.228 | 0.9903 |
| | 500 | 20 | 0.257 | 0.9881 | 18 | 0.280 | 0.9861 |
| | 700 | 20 | 0.442 | 0.9627 | 17 | 0.477 | 0.9565 |
| | 1000 | 20 | 0.228 | 0.9906 | 18 | 0.251 | 0.9887 |
| nitrogen | 100 | 4 | 1.808 | 0.9818 | 4 | 1.808 | 0.9818 |
| | 300 | 7 | 1.400 | 0.9890 | 6 | 1.453 | 0.9882 |
| | 500 | 9 | 1.333 | 0.9901 | 8 | 1.405 | 0.9890 |
| | 700 | 10 | 1.077 | 0.9935 | 8 | 1.143 | 0.9929 |
| | 1000 | 8 | 0.856 | 0.9960 | 7 | 0.898 | 0.9958 |

Notes:

| | |
|----------------|---|
| P* | Absolute pressure, mm Hg |
| PRESS | Predicted Residual Error Sum of Squares |
| p | F-statistic probability |
| F | Number of factors in calibration model |
| SECV | Standard Error of Cross Validation |
| R ² | Squared correlation coefficient |

**TABLE A-4. FT-IR Calibration on Natural Gas Components
Based on GC Analysis of Synthetic Blend of Standards**

| <u>Compound</u> | <u>P* (abs) mm Hg</u> | <u>at min. PRESS</u> | | | <u>at $p \leq 0.75$</u> | | |
|-----------------|---------------------------|----------------------|-------------|----------------------|------------------------------------|-------------|----------------------|
| | | <u>F</u> | <u>SECV</u> | <u>R²</u> | <u>F</u> | <u>SECV</u> | <u>R²</u> |
| methane | 100 | 4 | 1.545 | 0.9905 | 4 | 1.545 | 0.9905 |
| | 300 | 7 | 1.350 | 0.9928 | 6 | 1.410 | 0.9922 |
| | 500 | 10 | 1.230 | 0.9940 | 8 | 1.319 | 0.9931 |
| | 700 | 10 | 0.962 | 0.9964 | 8 | 1.032 | 0.9960 |
| | 1000 | 13 | 0.823 | 0.9973 | 8 | 0.899 | 0.9969 |
| ethane | 100 | 15 | 0.183 | 0.9984 | 12 | 0.202 | 0.9980 |
| | 300 | 9 | 0.254 | 0.9969 | 7 | 0.268 | 0.9966 |
| | 500 | 20 | 0.193 | 0.9982 | 16 | 0.205 | 0.9980 |
| | 700 | 16 | 0.224 | 0.9976 | 14 | 0.246 | 0.9971 |
| | 1000 | 10 | 0.227 | 0.9975 | 8 | 0.238 | 0.9973 |
| propane | 100 | 5 | 0.488 | 0.9983 | 4 | 0.524 | 0.9981 |
| | 300 | 20 | 0.479 | 0.9984 | 19 | 0.522 | 0.9981 |
| | 500 | 20 | 0.432 | 0.9987 | 17 | 0.467 | 0.9985 |
| | 700 | 20 | 0.709 | 0.9965 | 16 | 0.758 | 0.9960 |
| | 1000 | 19 | 0.498 | 0.9983 | 16 | 0.524 | 0.9981 |
| butane | 100 | 14 | 0.152 | 0.9957 | 11 | 0.158 | 0.9953 |
| | 300 | 18 | 0.223 | 0.9906 | 17 | 0.228 | 0.9903 |
| | 500 | 20 | 0.305 | 0.9828 | 14 | 0.335 | 0.9798 |
| | 700 | 20 | 0.470 | 0.9582 | 17 | 0.501 | 0.9526 |
| | 1000 | 19 | 0.282 | 0.9855 | 16 | 0.300 | 0.9836 |
| nitrogen | 100 | 4 | 1.775 | 0.9823 | 4 | 1.775 | 0.9823 |
| | 300 | 7 | 1.400 | 0.9890 | 6 | 1.453 | 0.9882 |
| | 500 | 10 | 1.263 | 0.9910 | 8 | 1.364 | 0.9895 |
| | 700 | 10 | 1.040 | 0.9940 | 8 | 1.075 | 0.9937 |
| | 1000 | 10 | 0.912 | 0.9953 | 7 | 0.959 | 0.9952 |

Notes:

| | |
|----------------|---|
| P* | Absolute pressure, mm Hg |
| PRESS | Predicted Residual Error Sum of Squares |
| p | F-statistic probability |
| F | Number of Factors in calibration model |
| SECV | Standard Error of Cross Validation |
| R ² | Squared correlation coefficient |

TABLE A-5. GC Analysis of a Scott Natural Gas Standard

| compound | known mol % | GC mol % | ASTM repeatability | GC stds | residual error (known-GC) | error % |
|----------|----------------|-------------|-----------------------|------------|------------------------------|---------|
| methane | 88.68 | 88.81 | 0.30 | 0.30 | -0.13 | -0.15 |
| ethane | 3.50 | 3.48 | 0.05 | 0.05 | 0.02 | 0.57 |
| propane | 1.00 | 0.99 | 0.03 | 0.03 | 0.01 | 1.00 |
| butane | 0.40 | 0.38 | 0.03 | 0.38 | 0.01 | 2.50 |

GC = average result of 15 measurements

stds = sample standard deviation of 15 measurements

error % = $100 \times (\text{arithmetic difference} / \text{known})$

TABLE A-6a. Validation of Calibration Models for Natural Gas Components

FT-IR Cell Pressure = 100 mm Hg, abs

| Sample FTIR ID | Methane | | | Ethane | | | Propane | | | n-Butane | | | Nitrogen | | |
|-------------------|---------|-------|---------------------|--------|-------|---------------------|---------|-------|---------------------|----------|-------|---------------------|----------|-------|---------------------|
| | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 |
| val04p1 | 94.74 | 93.92 | 0.82 | 94.33 | 94.75 | -0.42 | 2.74 | 3.09 | -0.34 | 2.91 | 0.37 | 0.49 | 0.04 | 0.95 | 0.49 |
| val05p1 | 94.55 | 94.94 | -0.39 | 94.75 | 94.75 | 0.00 | 2.95 | 3.14 | -0.19 | 3.04 | 0.40 | 0.21 | 0.06 | 0.83 | 0.45 |
| val06p1 | 94.73 | 95.76 | -1.03 | 95.24 | 94.73 | 0.51 | 2.74 | 2.89 | -0.14 | 2.81 | 0.37 | 0.65 | 0.04 | 0.90 | 0.47 |
| val07p1 | 88.78 | 89.34 | -0.56 | 89.06 | 89.06 | 0.00 | 3.53 | 3.57 | -0.04 | 3.55 | 1.02 | 0.82 | 0.40 | 1.62 | 1.01 |
| val08p1 | 90.10 | 91.36 | -1.26 | 90.73 | 90.73 | 0.00 | 5.98 | 6.29 | -0.31 | 6.14 | 0.25 | 0.60 | 0.10 | 0.74 | 0.42 |
| val09p1 | 96.37 | 97.87 | -1.49 | 97.12 | 97.12 | 0.00 | 1.94 | 2.12 | -0.18 | 2.03 | 0.20 | 0.23 | 0.00 | 0.12 | 0.06 |
| val10p1 | 88.78 | 89.88 | -1.10 | 89.33 | 89.33 | 0.00 | 3.53 | 3.54 | -0.01 | 3.54 | 1.02 | 0.89 | 0.40 | 1.21 | 0.81 |
| val11p1 | 84.98 | 86.33 | -1.35 | 85.66 | 85.66 | 0.00 | 6.50 | 6.81 | -0.31 | 6.66 | 3.00 | 2.86 | 0.30 | 1.09 | 0.70 |
| val12p1 | 88.68 | 90.05 | -1.37 | 89.36 | 89.36 | 0.00 | 3.50 | 3.54 | -0.04 | 3.52 | 1.00 | 0.78 | 0.40 | 1.22 | 0.81 |
| average | ----- | ----- | -0.86 | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| sids | ----- | ----- | 0.73 | ----- | ----- | 0.13 | ----- | ----- | 0.30 | ----- | ----- | ----- | ----- | 0.29 | 1.27 |

FT-IR Cell Pressure = 300 mm Hg, abs

| Sample FTIR ID | Methane | | | Ethane | | | Propane | | | n-Butane | | | Nitrogen | | |
|-------------------|---------|-------|---------------------|--------|-------|---------------------|---------|-------|---------------------|----------|-------|---------------------|----------|-------|---------------------|
| | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 |
| val04p2 | 94.74 | 95.04 | -0.30 | 94.89 | 95.08 | -0.19 | 2.74 | 2.99 | -0.25 | 2.86 | 0.37 | 0.00 | 0.04 | 0.17 | 0.10 |
| val05p2 | 94.55 | 95.61 | -1.06 | 95.08 | 95.08 | 0.00 | 2.95 | 2.95 | -0.00 | 2.95 | 0.40 | 0.00 | 0.06 | 0.16 | 0.11 |
| val06p2 | 94.73 | 94.95 | -0.22 | 94.84 | 94.73 | 0.11 | 2.74 | 2.75 | -0.01 | 2.75 | 0.37 | 0.00 | 0.04 | 0.21 | 0.12 |
| val07p2 | 88.78 | ND | ND | 44.39 | ND | ND | 3.53 | ND | ND | 1.77 | 1.02 | ND | 0.40 | ND | 0.20 |
| val08p2 | 90.10 | 90.57 | -0.47 | 90.34 | 90.57 | -0.23 | 5.98 | 6.14 | -0.16 | 6.06 | 0.25 | 0.00 | 0.10 | 0.87 | 0.49 |
| val09p2 | 96.37 | 96.11 | 0.27 | 96.24 | 96.11 | 0.07 | 1.94 | 2.18 | -0.24 | 2.06 | 0.20 | 0.00 | 0.00 | 0.07 | 0.04 |
| val10p2 | 88.78 | 89.41 | -0.63 | 89.09 | 89.09 | 0.00 | 3.53 | 3.45 | 0.08 | 3.49 | 1.02 | 0.00 | 0.40 | 1.23 | 0.82 |
| val11p2 | 84.98 | 85.82 | -0.84 | 85.40 | 85.40 | 0.00 | 6.50 | 6.59 | -0.09 | 6.55 | 3.00 | 1.84 | 0.30 | 1.14 | 0.72 |
| val12p2 | 88.68 | 89.27 | -0.59 | 88.97 | 88.97 | 0.00 | 3.50 | 3.43 | 0.07 | 3.47 | 1.00 | 0.00 | 0.40 | 1.28 | 0.84 |
| average | ----- | ----- | -0.43 | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| sids | ----- | ----- | 0.41 | ----- | ----- | 0.12 | ----- | ----- | 0.40 | ----- | ----- | ----- | ----- | 0.39 | 1.31 |

FT-IR Cell Pressure = 500 mm Hg, abs

| Sample FTIR ID | Methane | | | Ethane | | | Propane | | | n-Butane | | | Nitrogen | | |
|-------------------|---------|-------|---------------------|--------|-------|---------------------|---------|-------|---------------------|----------|-------|---------------------|----------|-------|---------------------|
| | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 | GC | FTIR | GC-FTIR (GC+FTIR)/2 |
| val04p3 | 94.74 | 95.08 | -0.34 | 94.91 | 94.65 | 0.26 | 2.74 | 2.99 | -0.25 | 2.87 | 0.37 | 0.40 | 0.04 | 0.12 | 0.08 |
| val05p3 | 94.55 | 94.76 | -0.21 | 94.65 | 94.65 | 0.00 | 2.95 | 2.89 | 0.06 | 2.92 | 0.40 | 0.55 | 0.06 | 0.00 | 0.03 |
| val06p3 | 94.73 | 95.41 | -0.68 | 95.07 | 94.73 | 0.34 | 2.74 | 2.93 | -0.19 | 2.83 | 0.37 | 0.51 | 0.04 | 0.00 | 0.04 |
| val07p3 | 88.78 | 88.22 | 0.56 | 88.50 | 88.50 | 0.00 | 3.53 | 3.49 | 0.05 | 3.51 | 1.02 | 1.82 | 0.40 | 1.10 | 0.75 |
| val08p3 | 90.10 | 90.21 | -0.11 | 90.16 | 90.16 | 0.00 | 5.98 | 6.16 | -0.18 | 6.07 | 0.25 | 0.77 | 0.10 | 0.87 | 0.48 |
| val09p3 | 96.37 | 96.76 | -0.39 | 96.57 | 96.57 | 0.00 | 1.94 | 2.11 | -0.17 | 2.02 | 0.20 | 0.00 | 0.00 | 0.23 | 0.12 |
| val10p3 | 88.78 | 88.51 | 0.27 | 88.64 | 88.64 | 0.00 | 3.53 | 3.43 | 0.10 | 3.48 | 1.02 | 0.98 | 0.40 | 1.46 | 0.93 |
| val11p3 | 84.98 | 84.84 | 0.14 | 84.91 | 84.91 | 0.00 | 6.50 | 6.72 | -0.22 | 6.61 | 3.00 | 3.42 | 0.30 | 1.21 | 0.78 |
| val12p3 | 88.68 | 88.71 | -0.03 | 88.69 | 88.69 | 0.00 | 3.50 | 3.41 | 0.09 | 3.46 | 1.00 | 1.04 | 0.40 | 1.38 | 0.89 |
| average | ----- | ----- | -0.09 | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| sids | ----- | ----- | 0.3735 | ----- | ----- | 0.1474 | ----- | ----- | 0.3149 | ----- | ----- | ----- | ----- | 0.51 | 1.3210 |

Notes:

GC = GC calibration data

GC - FTIR = arithmetic difference = residual error

ND = no data
c:\lngas95.wb3\kc_sum

sids = sample standard deviation

FTIR = FT-IR derived validation data

TABLE A-6b. Validation of Calibration Models for Natural Gas Components

FT-IR Cell Pressure = 700 mm Hg, abs

| Sample FTIR ID | Methane | | | Ethane | | | Propane | | | n-Butane | | | Nitrogen | | |
|-------------------|---------|-------|---------------------|--------|------|---------------------|---------|------|---------------------|----------|-------|---------------------|----------|------|---------------------|
| | GC | FTIR | GC-FTIR [GC+FTIR]/2 | GC | FTIR | GC-FTIR [GC+FTIR]/2 | GC | FTIR | GC-FTIR [GC+FTIR]/2 | GC | FTIR | GC-FTIR [GC+FTIR]/2 | GC | FTIR | GC-FTIR [GC+FTIR]/2 |
| val04p4 | 94.74 | 95.57 | -0.83 | 95.15 | 2.74 | 3.08 | -0.34 | 2.91 | 0.37 | 0.79 | -0.42 | 0.58 | 0.04 | 0.08 | 0.06 |
| val05p4 | 94.55 | 95.82 | -1.27 | 95.19 | 2.95 | 3.11 | -0.16 | 3.03 | 0.40 | 0.60 | -0.20 | 0.50 | 0.06 | 0.24 | 0.15 |
| val06p4 | 94.73 | 95.59 | -0.85 | 95.16 | 2.74 | 2.94 | -0.20 | 2.84 | 0.37 | 0.68 | -0.31 | 0.52 | 0.04 | 0.09 | 0.06 |
| val07p4 | 88.78 | 88.77 | 0.01 | 88.77 | 3.53 | 3.62 | -0.09 | 3.58 | 1.02 | 2.21 | -1.19 | 1.61 | 0.40 | 0.44 | 0.04 |
| val08p4 | 90.10 | 91.95 | -1.85 | 91.03 | 5.98 | 6.24 | -0.25 | 6.11 | 0.25 | 2.06 | -1.81 | 1.16 | 0.10 | 0.43 | 0.26 |
| val09p4 | 96.37 | 97.27 | -0.90 | 96.82 | 1.94 | 2.10 | -0.16 | 2.02 | 0.20 | 0.80 | -0.60 | 0.50 | 0.00 | 0.00 | 0.00 |
| val10p4 | 88.78 | 90.45 | -1.67 | 89.61 | 3.53 | 3.54 | -0.01 | 3.54 | 1.02 | 2.18 | -1.16 | 1.60 | 0.40 | 0.81 | 0.61 |
| val11p4 | 84.98 | 86.61 | -1.63 | 85.79 | 6.50 | 6.52 | -0.02 | 6.51 | 3.00 | 4.66 | -1.66 | 3.83 | 0.30 | 0.50 | 0.40 |
| val12p4 | 88.68 | 90.56 | -1.89 | 89.62 | 3.50 | 3.59 | -0.09 | 3.55 | 1.00 | 1.89 | -0.89 | 1.45 | 0.40 | 0.88 | 0.64 |
| average | | | -1.21 | | | | -0.15 | | | | -0.91 | | | | |
| stds | | | 0.62 | | | | 0.11 | | | | 0.58 | | | | |

FT-IR Cell Pressure = 1,000 mm Hg, abs

| Sample FTIR ID | Methane | | | Ethane | | | Propane | | | n-Butane | | | Nitrogen | | |
|-------------------|---------|-------|---------------------|--------|------|---------------------|---------|------|---------------------|----------|-------|---------------------|----------|------|---------------------|
| | GC | FTIR | GC-FTIR [GC+FTIR]/2 | GC | FTIR | GC-FTIR [GC+FTIR]/2 | GC | FTIR | GC-FTIR [GC+FTIR]/2 | GC | FTIR | GC-FTIR [GC+FTIR]/2 | GC | FTIR | GC-FTIR [GC+FTIR]/2 |
| val04p5 | 94.74 | 94.22 | 0.52 | 94.48 | 2.74 | 3.26 | -0.52 | 3.00 | 0.37 | 0.26 | 0.11 | 0.32 | 0.04 | 0.30 | 0.17 |
| val05p5 | 94.55 | 95.28 | -0.73 | 94.92 | 2.95 | 3.26 | -0.31 | 3.10 | 0.40 | 0.07 | 0.33 | 0.24 | 0.06 | 0.32 | 0.19 |
| val06p5 | 94.73 | 94.65 | 0.08 | 94.69 | 2.74 | 2.96 | -0.22 | 2.85 | 0.37 | 0.23 | 0.14 | 0.30 | 0.04 | 0.22 | 0.13 |
| val07p5 | 88.78 | 87.19 | 1.59 | 87.98 | 3.53 | 3.85 | -0.32 | 3.69 | 1.02 | 2.10 | -1.08 | 1.56 | 0.40 | 1.22 | 0.81 |
| val08p5 | 90.10 | 89.60 | 0.50 | 89.85 | 5.98 | 6.57 | -0.59 | 6.27 | 0.25 | 0.48 | -0.23 | 0.37 | 0.10 | 0.84 | 0.47 |
| val09p5 | 96.37 | 96.17 | 0.20 | 96.27 | 1.94 | 2.19 | -0.25 | 2.07 | 0.20 | 0.05 | 0.15 | 0.13 | 0.00 | 0.38 | 0.19 |
| val10p5 | 88.78 | 87.88 | 0.90 | 88.33 | 3.53 | 4.02 | -0.49 | 3.77 | 1.02 | 1.24 | -0.22 | 1.13 | 0.40 | 1.56 | 0.98 |
| val11p5 | 84.98 | 80.46 | 4.53 | 82.72 | 6.50 | 7.26 | -0.76 | 6.88 | 3.00 | 4.48 | -1.48 | 3.74 | 0.30 | 0.35 | 0.33 |
| val12p5 | 88.68 | 89.24 | -0.56 | 88.96 | 3.50 | 3.87 | -0.37 | 3.69 | 1.00 | 1.44 | -0.44 | 1.22 | 0.40 | 1.42 | 0.91 |
| average | | | 0.78 | | | | -0.42 | | | | -0.30 | | | | |
| stds | | | 1.57 | | | | 0.18 | | | | 0.61 | | | | |

Notes:

GC = GC calibration data

FTIR = FT-IR derived validation data

GC - FTIR = arithmetic difference = residual error

stds = sample standard deviation

ND = no data

c:\ngas95.wb3\kc_sum

APPENDIX B

Figures

| | | |
|------|--|----|
| B-1 | FT-IR spectrum of methane (P=100 mm Hg) | 25 |
| B-2 | FT-IR spectrum of ethane (P=100 mm Hg) | 26 |
| B-3 | FT-IR spectrum of propane (P=100 mm Hg) | 27 |
| B-4 | FT-IR spectrum of butane (P=100 mm Hg) | 28 |
| B-5 | FT-IR spectrum of nitrogen (P=100 mm Hg) | 29 |
| B-6 | Effect of cell pressure on R^2 of calibration (F at min. PRESS; pressure-based analysis) | 30 |
| B-7 | Effect of cell pressure on R^2 of calibration (F at $p \leq 0.75$; pressure-based analysis) | 31 |
| B-8 | Calibration for methane at cell P=100 mm Hg (pressure based analysis) | 32 |
| B-9 | Calibration for ethane at cell P=100 mm Hg (pressure based analysis) | 33 |
| B-10 | Calibration for propane at cell P=100 mm Hg (pressure based analysis) | 34 |
| B-11 | Calibration for butane at cell P=100 mm Hg (pressure based analysis) | 35 |
| B-12 | Calibration for "nitrogen" at cell P=100 mm Hg (pressure based analysis) | 36 |
| B-13 | Effect of cell pressure on SECV for methane (pressure based analysis) | 37 |
| B-14 | Effect of cell pressure on SECV for ethane (pressure based analysis) | 38 |
| B-15 | Effect of cell pressure on SECV for propane (pressure based analysis) | 39 |
| B-16 | Effect of cell pressure on SECV for butane (pressure based analysis) | 40 |
| B-17 | Effect of cell pressure on SECV for "nitrogen" (pressure based analysis) | 41 |
| B-18 | Effect of cell pressure on the number of factors (F min. PRESS; pressure based analysis) | 42 |
| B-19 | Effect of cell pressure on the number of factors (F at $p \leq 0.75$; pressure based analysis) | 43 |
| B-20 | Effect of cell pressure on the residual error in validation | 44 |
| B-21 | Effect of cell pressure on the standard deviation of the residual error | 45 |
| B-22 | Limits of agreement for methane validation at cell pressure of 500 mm Hg, abs | 46 |
| B-23 | Limits of agreement for ethane validation at cell pressure of 500 mm Hg, abs | 47 |
| B-24 | Limits of agreement for propane validation at cell pressure of 500 mm Hg, abs | 48 |
| B-25 | Limits of agreement for butane validation at cell pressure of 500 mm Hg, abs | 49 |
| B-26 | Limits of agreement for "nitrogen" validation at cell pressure of 500 mm Hg, abs | 50 |

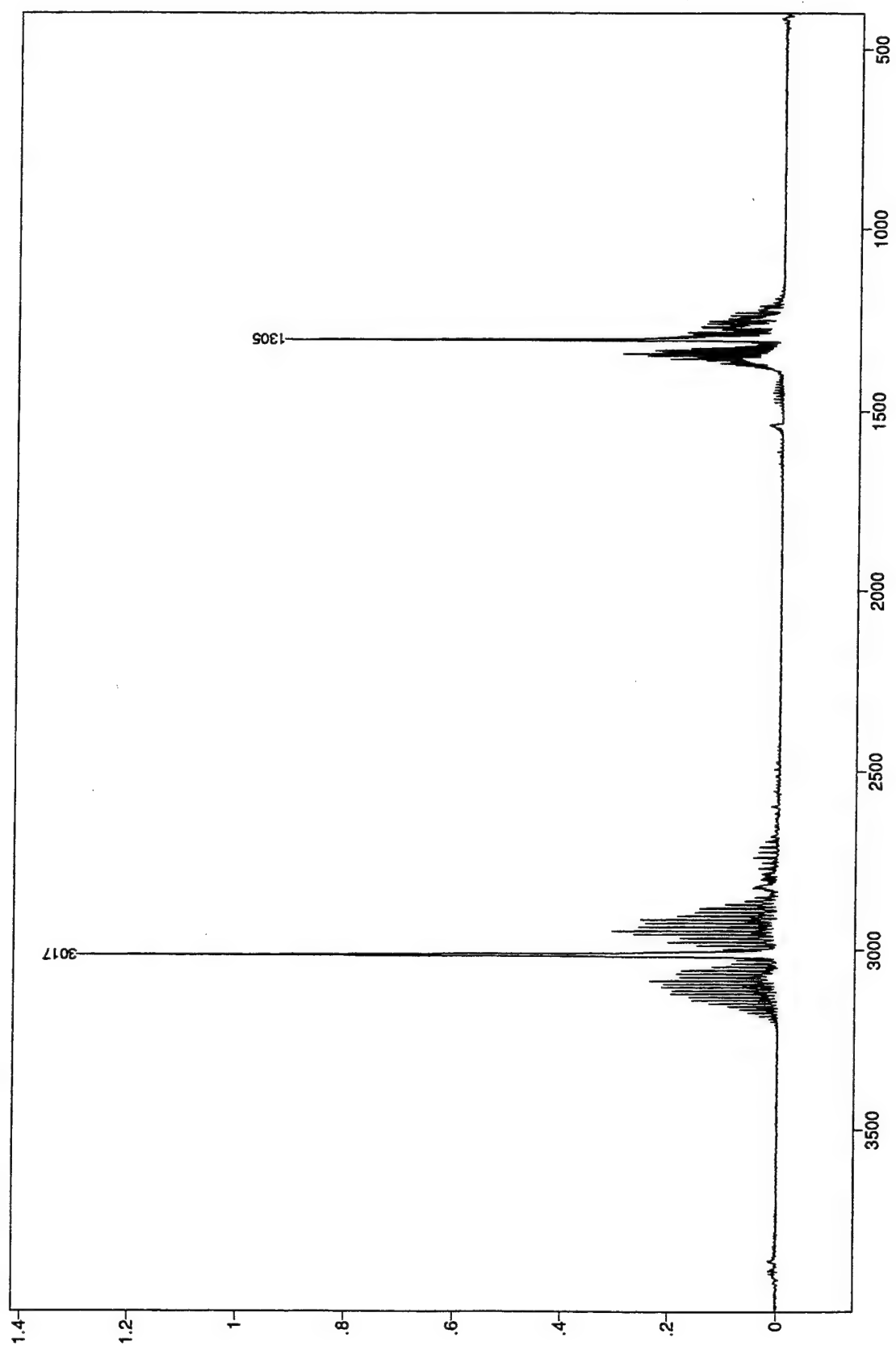


Figure B-1. FT-IR spectrum of methane (P=100 mm Hg)

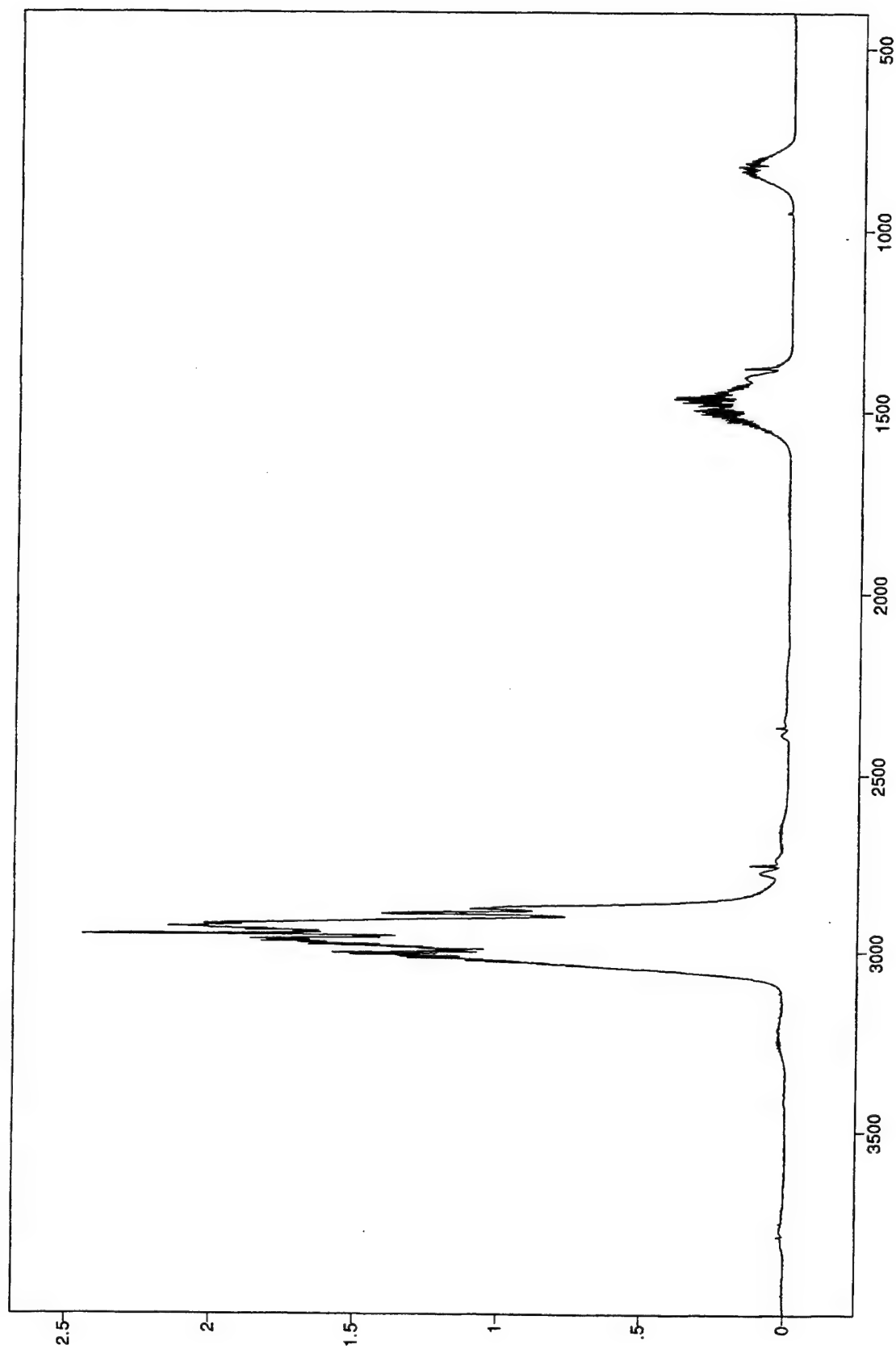


Figure B-2. FT-IR spectrum of ethane (P=100 mm Hg)

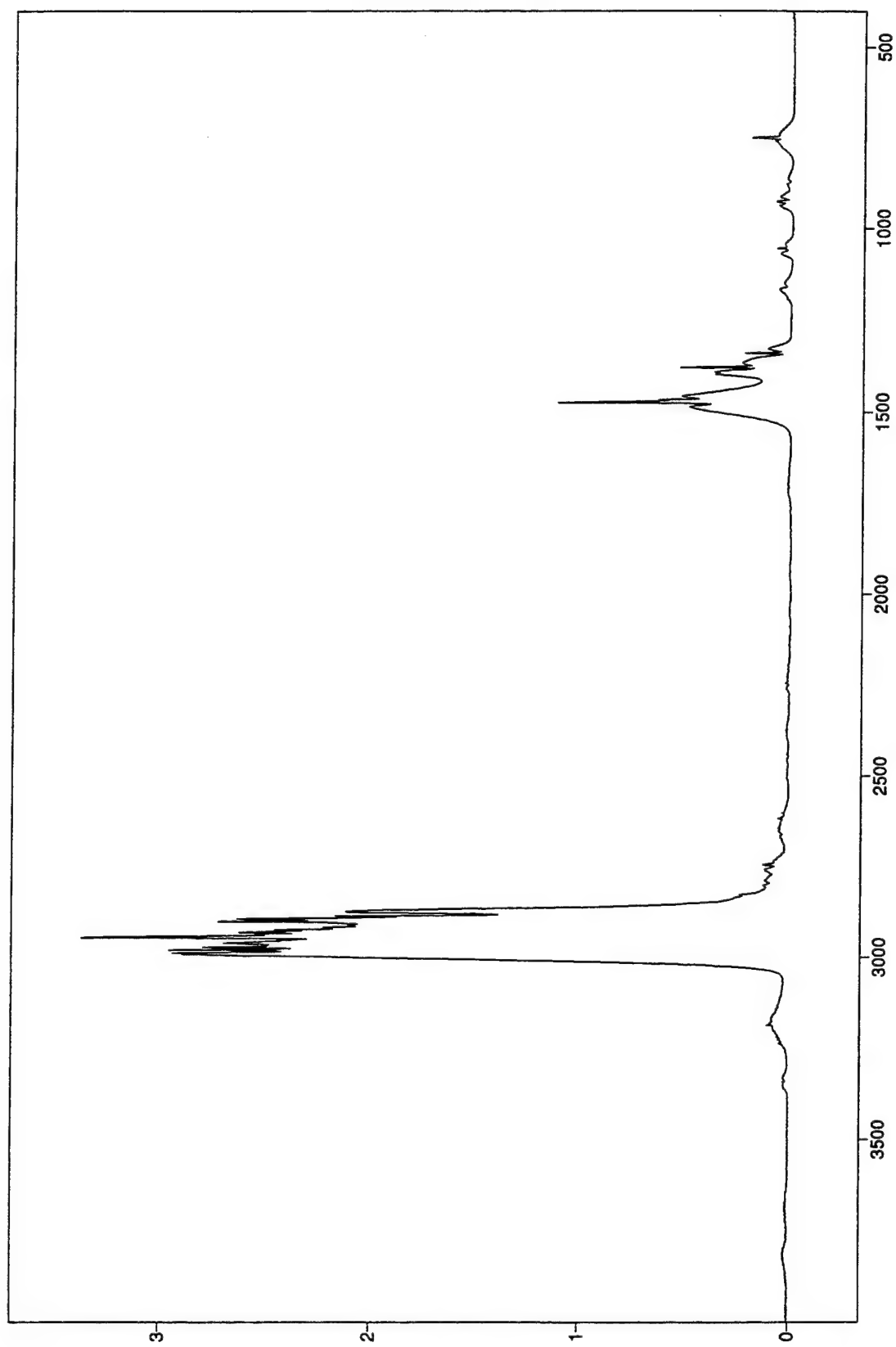


Figure B-3. FT-IR spectrum of propane (P=100 mm Hg)

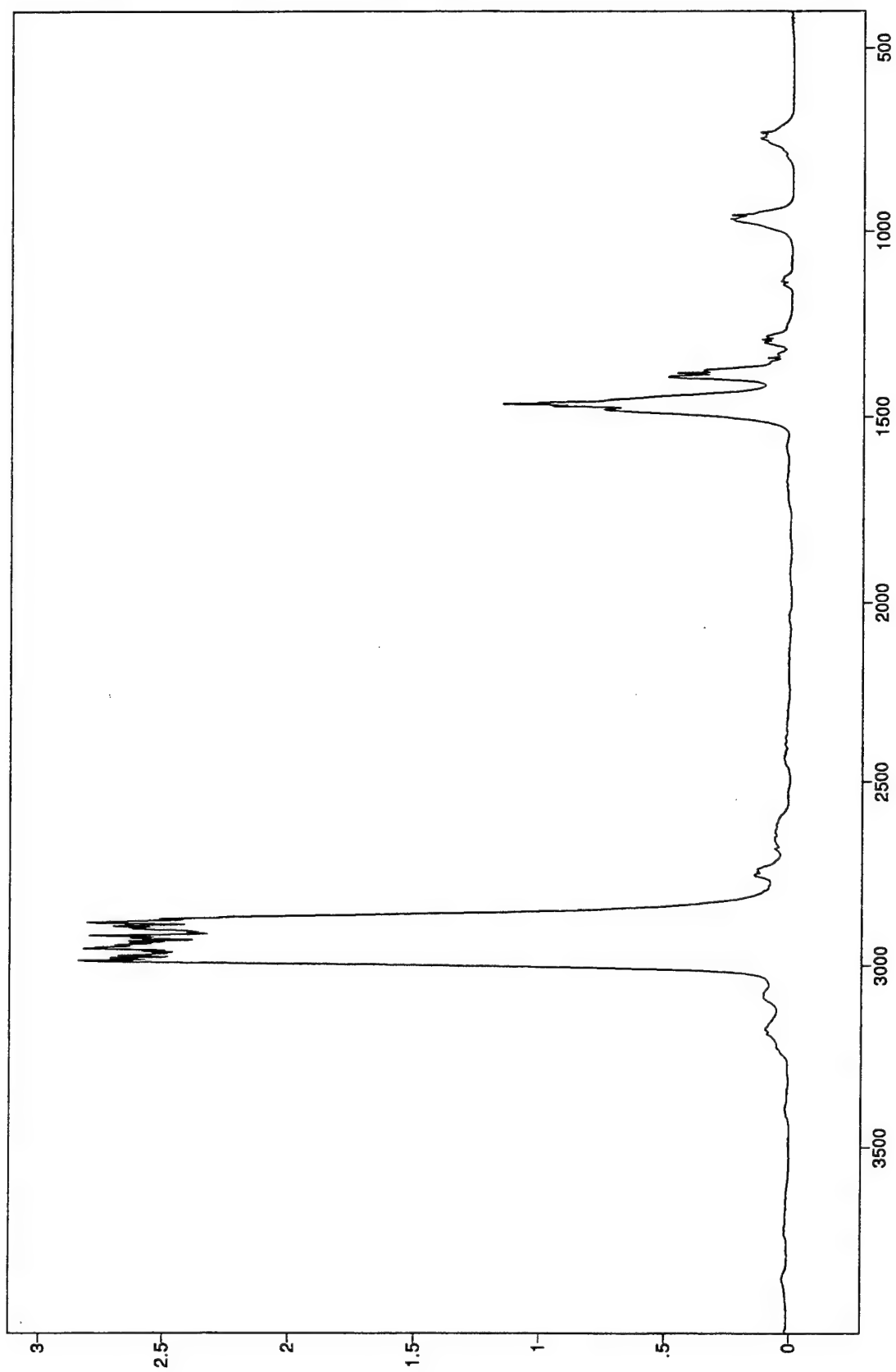


Figure B-4. FT-IR spectrum of butane (P=100 mm Hg).

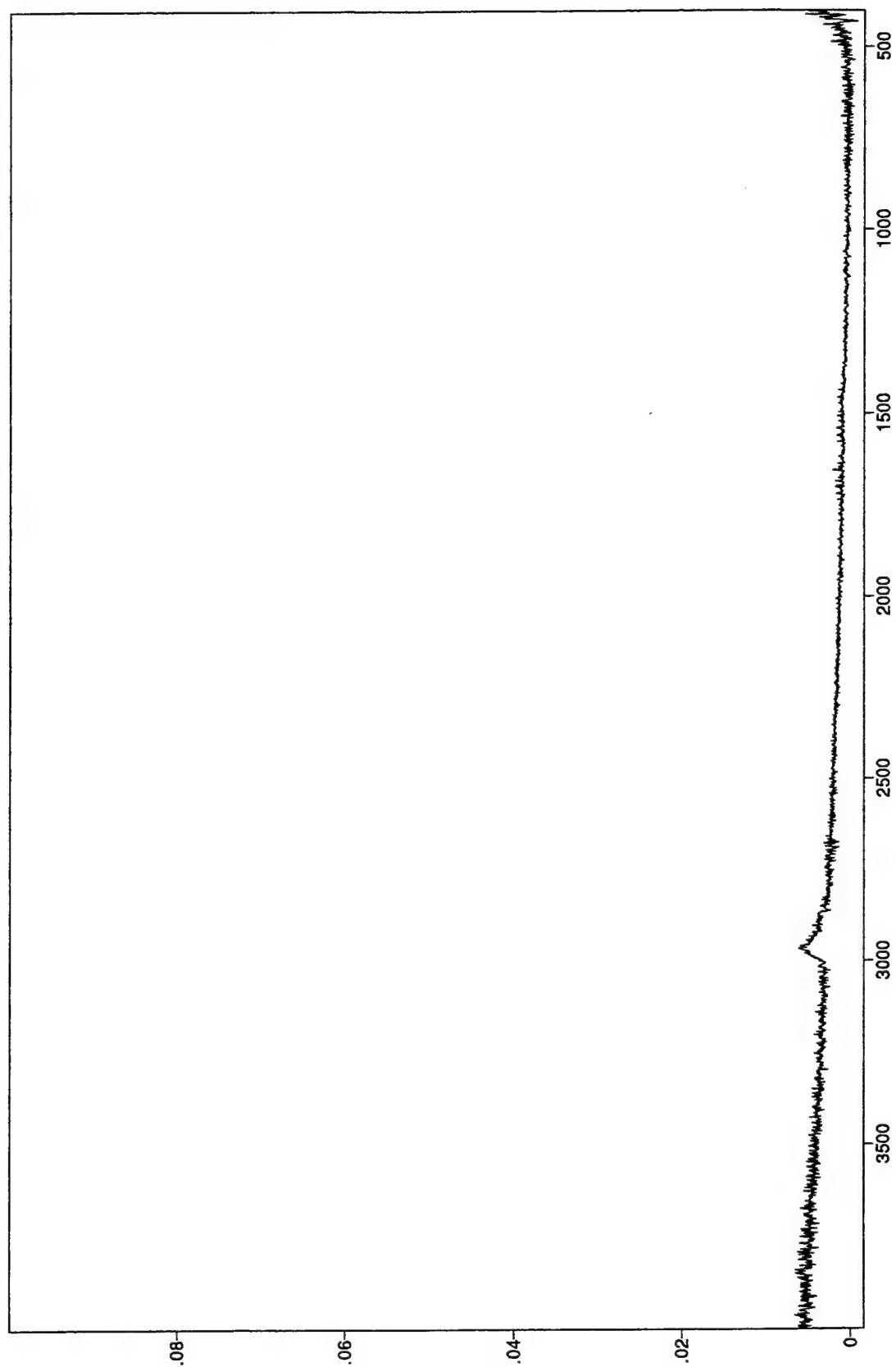


Figure B-5. FT-IR spectrum of nitrogen (P=100 mm Hg)

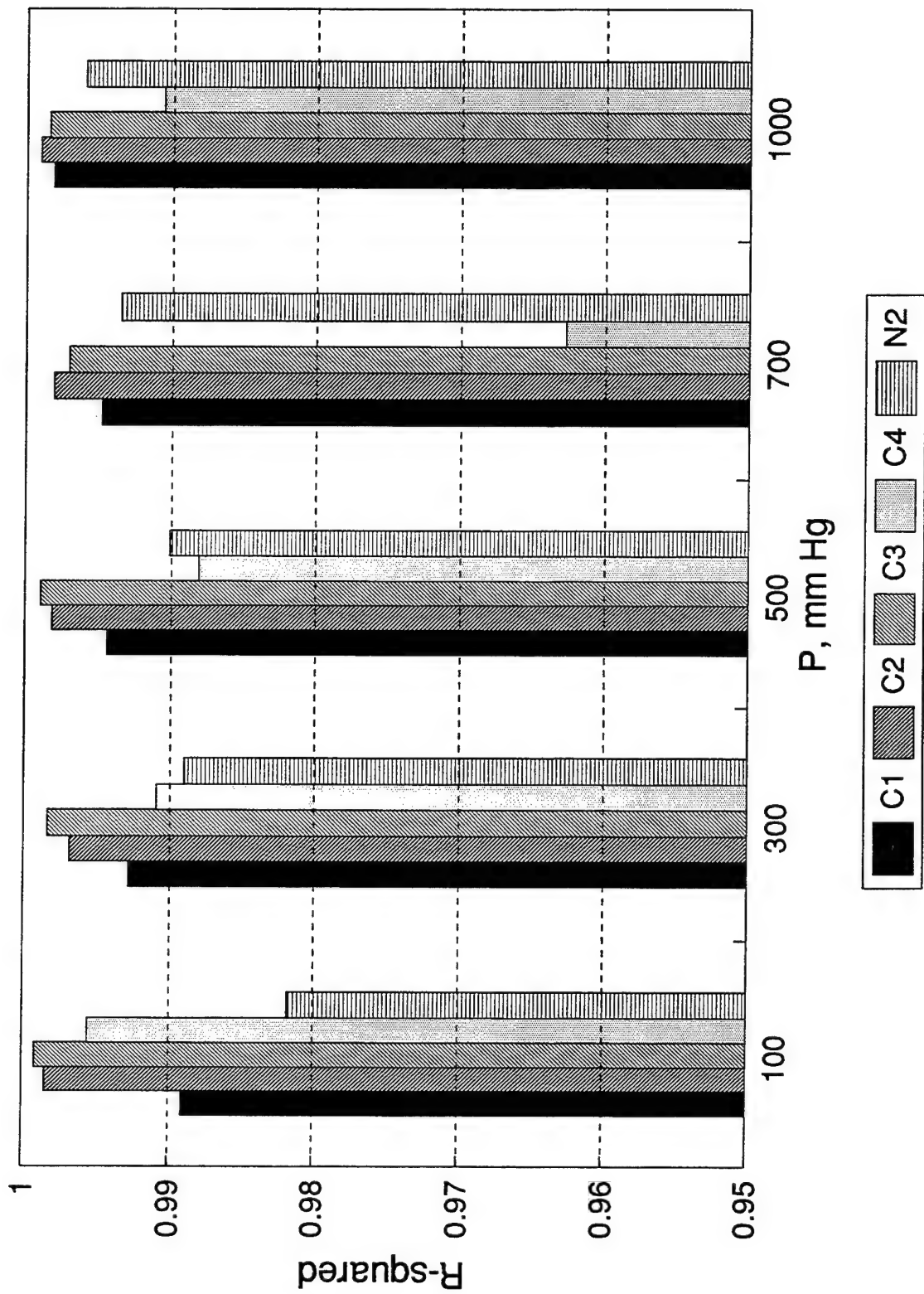


Figure B-6. Effect of cell pressure on R^2 of calibration (F at min. PRESS; pressure-based analysis)

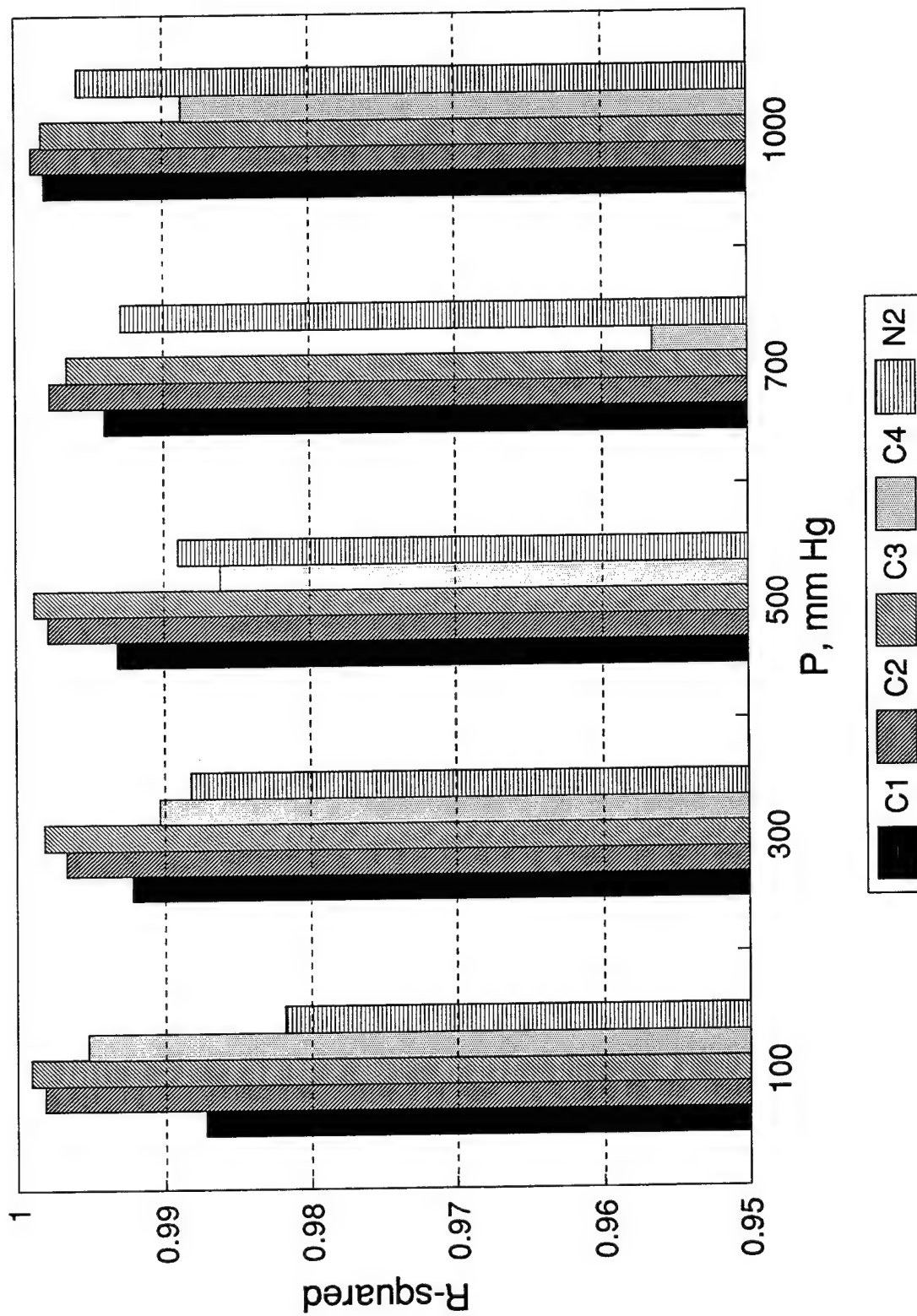


Figure B-7. Effect of cell pressure on R^2 of Calibration (F at $p \leq 0.75$; pressure-based analysis)

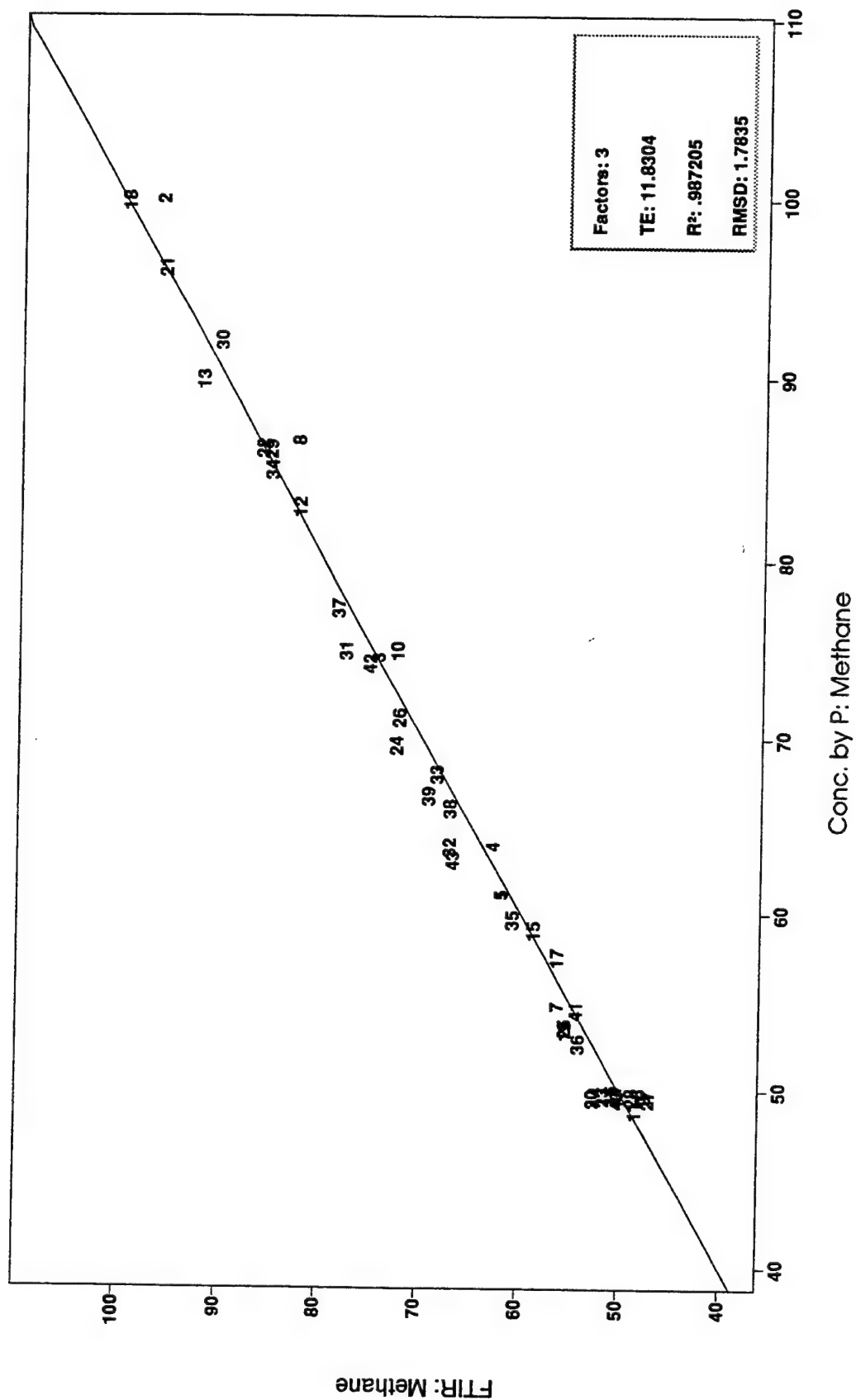


Figure B-8. Calibration for methane at cell P=100 mm Hg (pressure-based analysis)

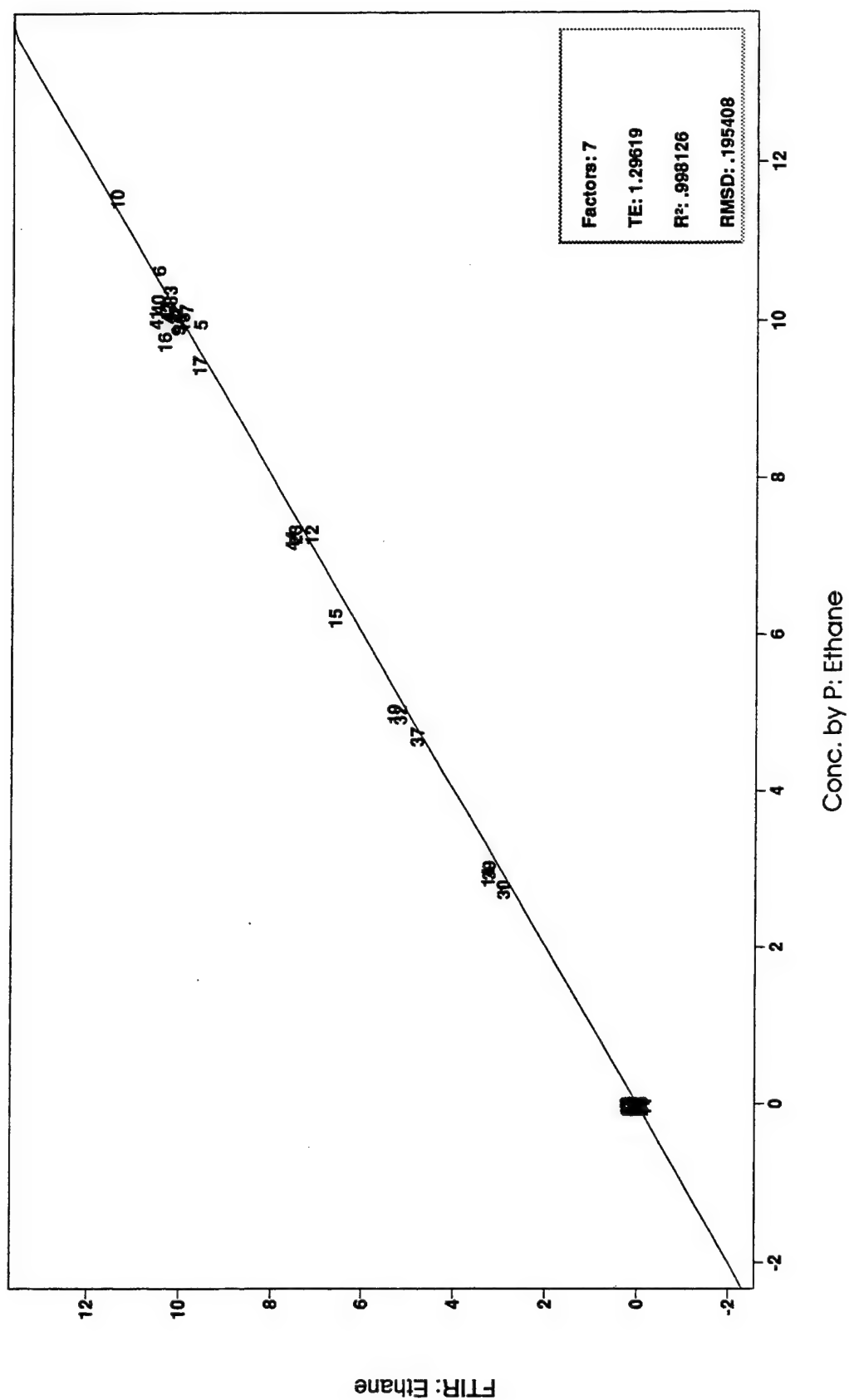


Figure B-9. Calibration for ethane at cell P=100 mm Hg (pressure-based analysis)

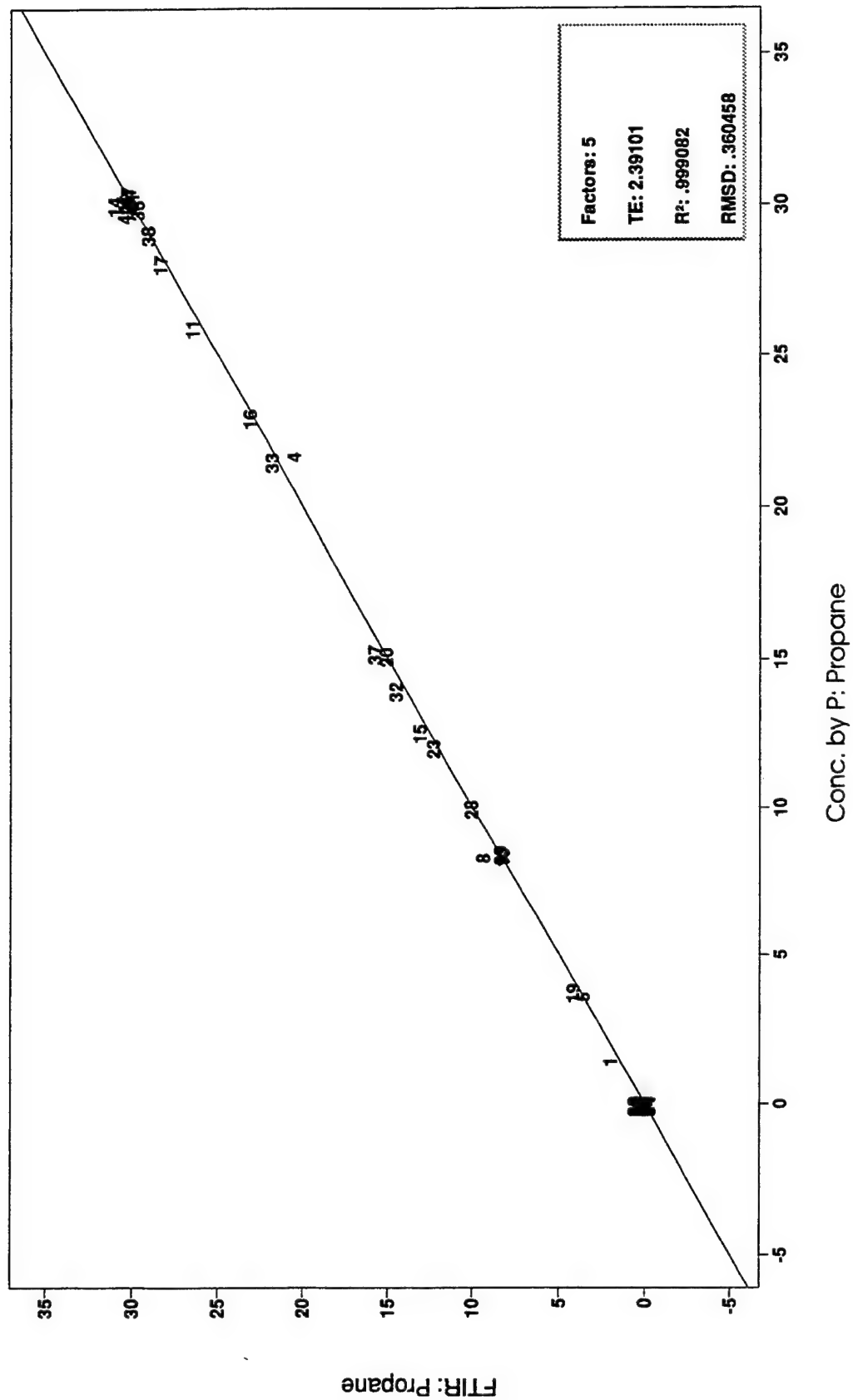


Figure B-10. Calibration for propane at cell P=100 mm Hg (pressure-based analysis)

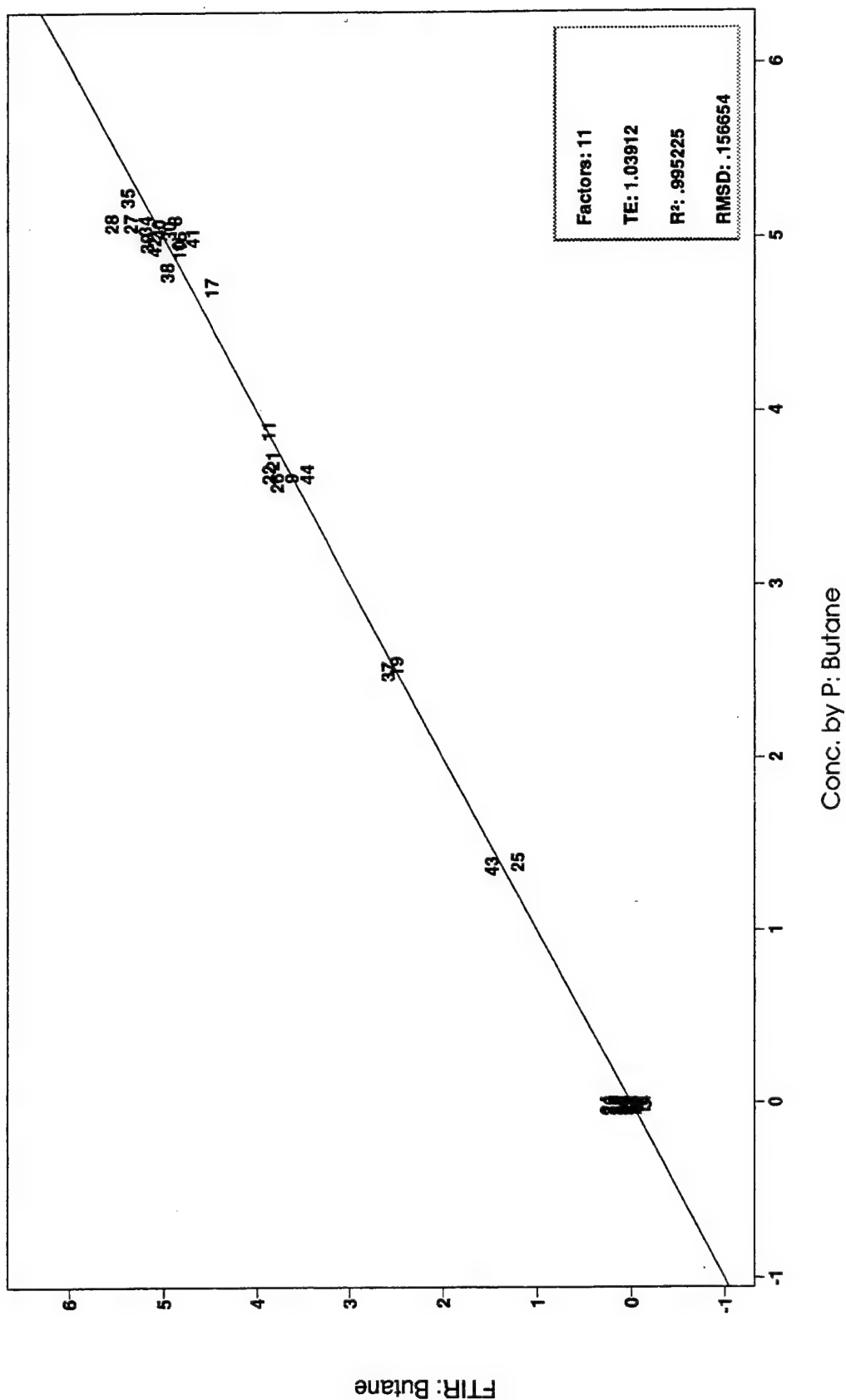


Figure B-11. Calibration for butane at cell P=100 mm Hg (pressure-based analysis)

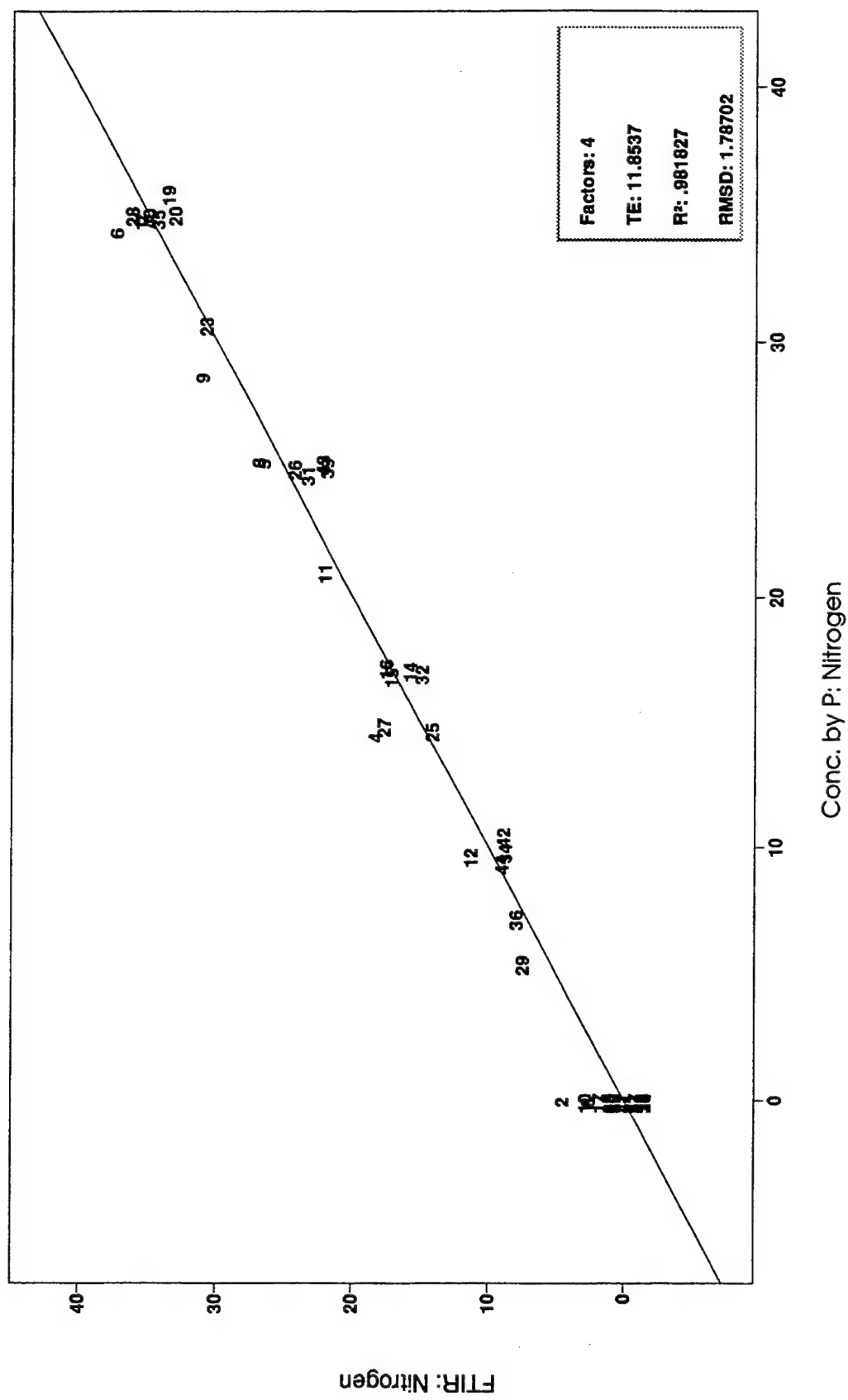


Figure B-12. Calibration for "nitrogen" at cell P=100 mm Hg (pressure-based analysis)

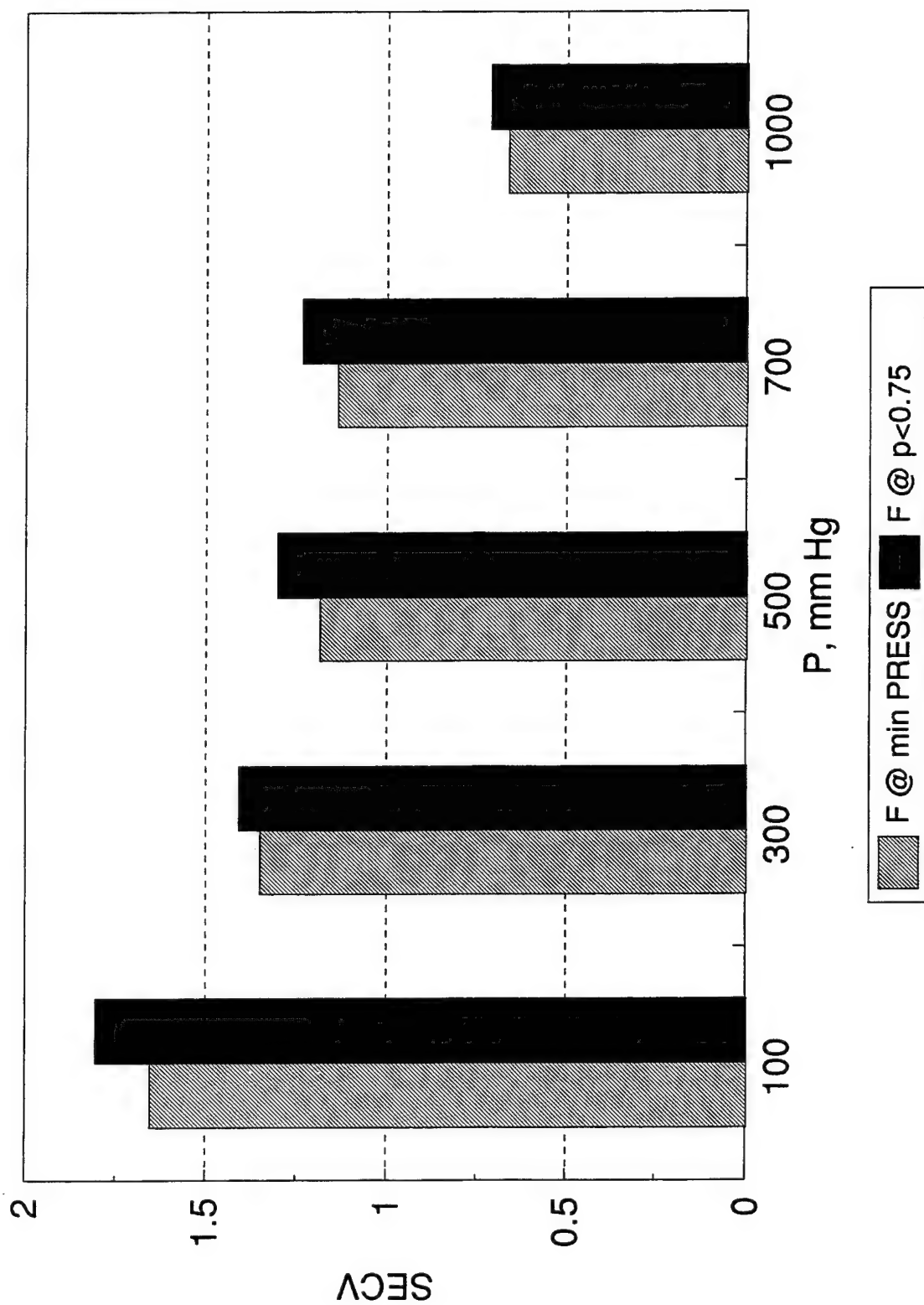


Figure B-13. Effect of cell pressure on SECV for methane (pressure-based analysis)

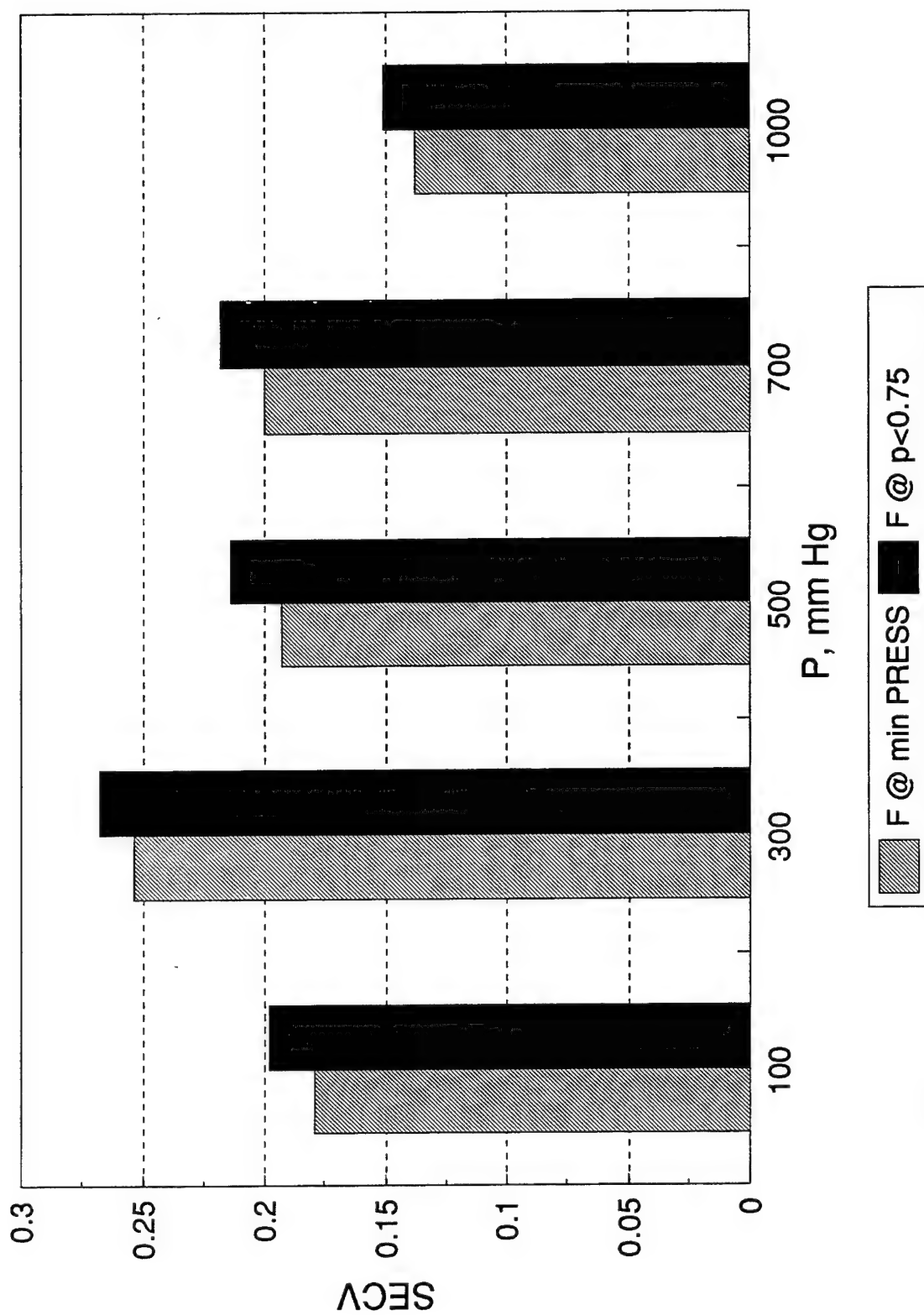


Figure B-14. Effect of cell pressure on SECv for ethane (pressure-based analysis)

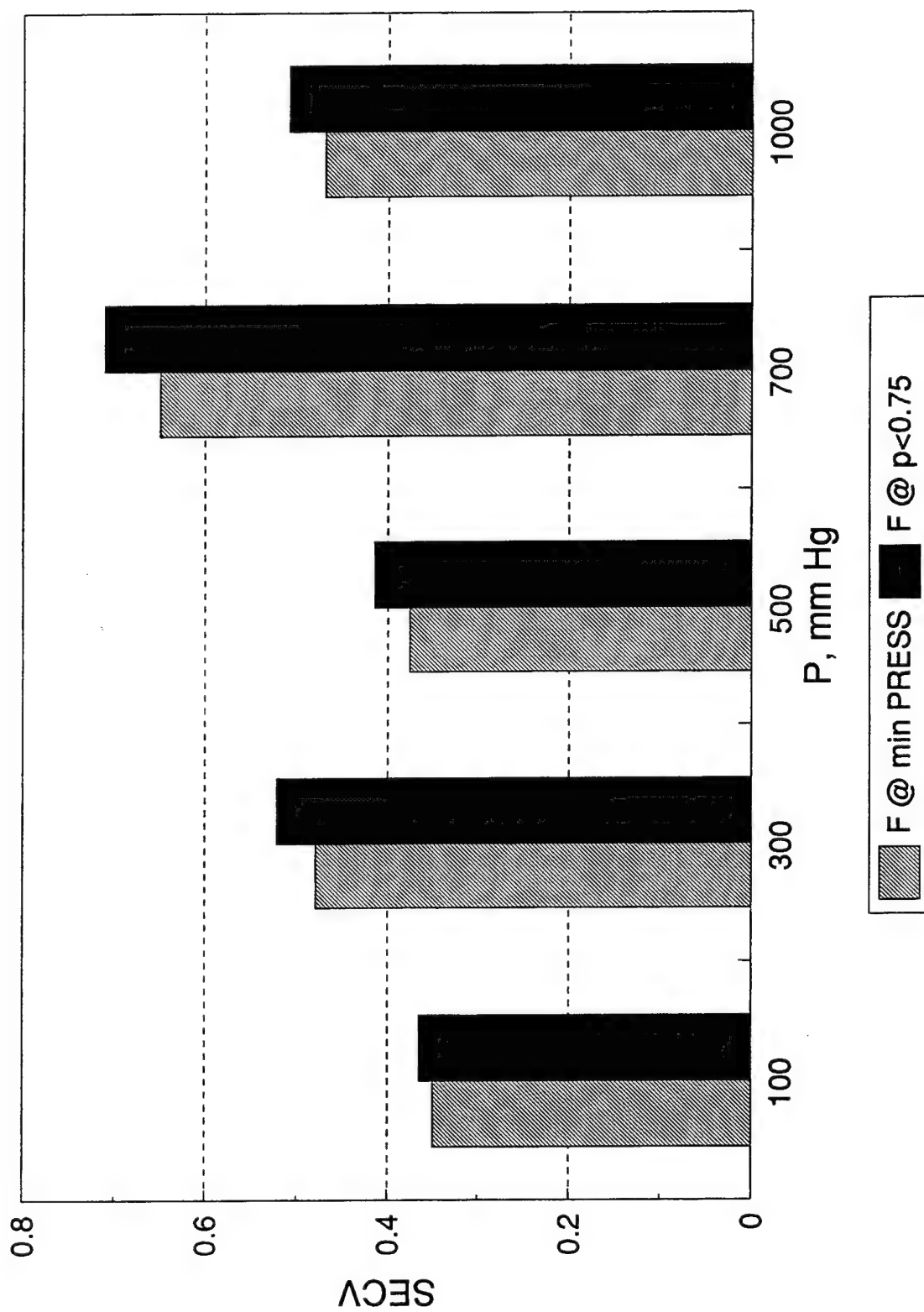


Figure B-15. Effect of cell pressure on SECY for propane (pressure-based analysis)

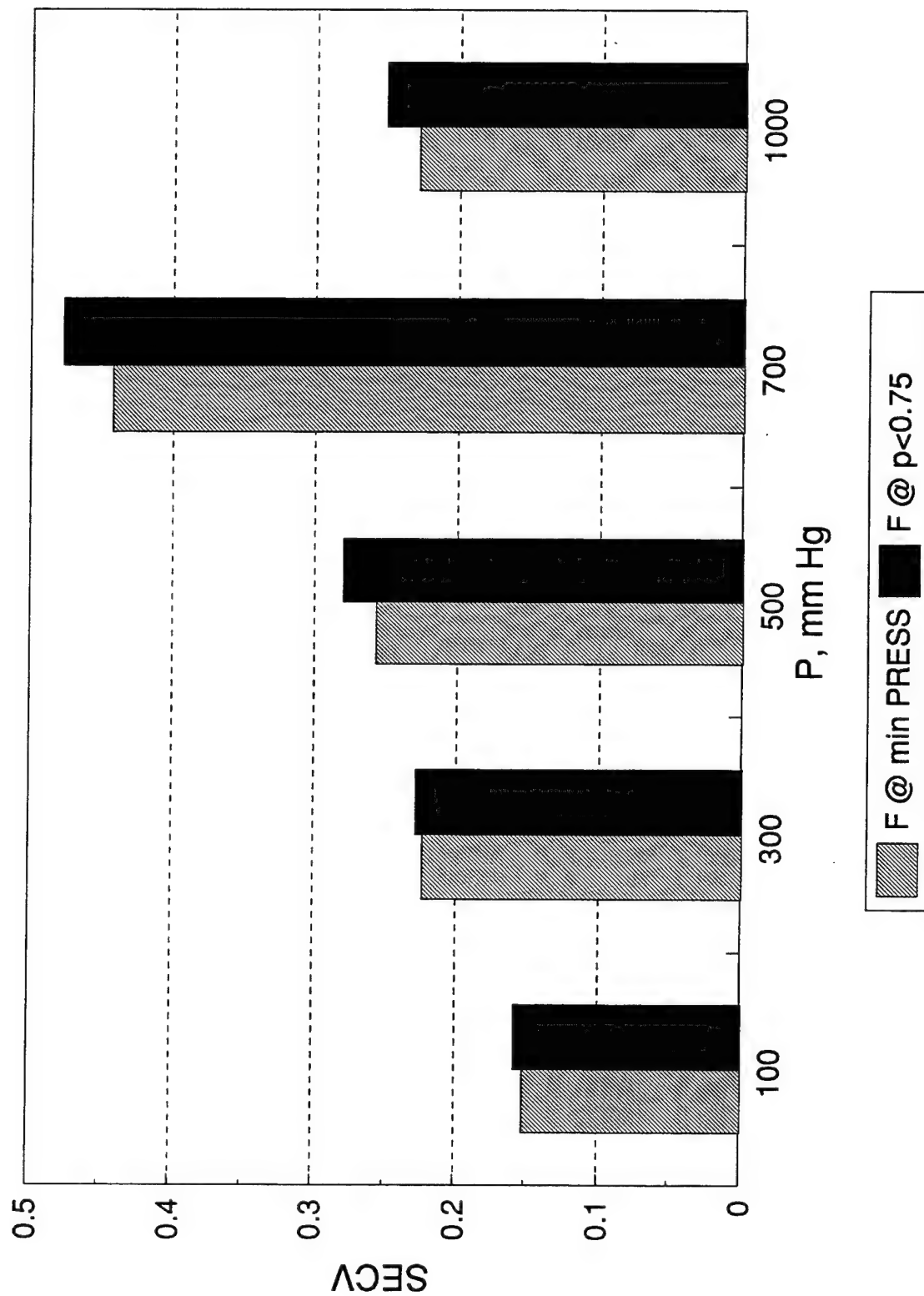


Figure B-16. Effect of cell pressure on SECv for butane (pressure-based analysis)

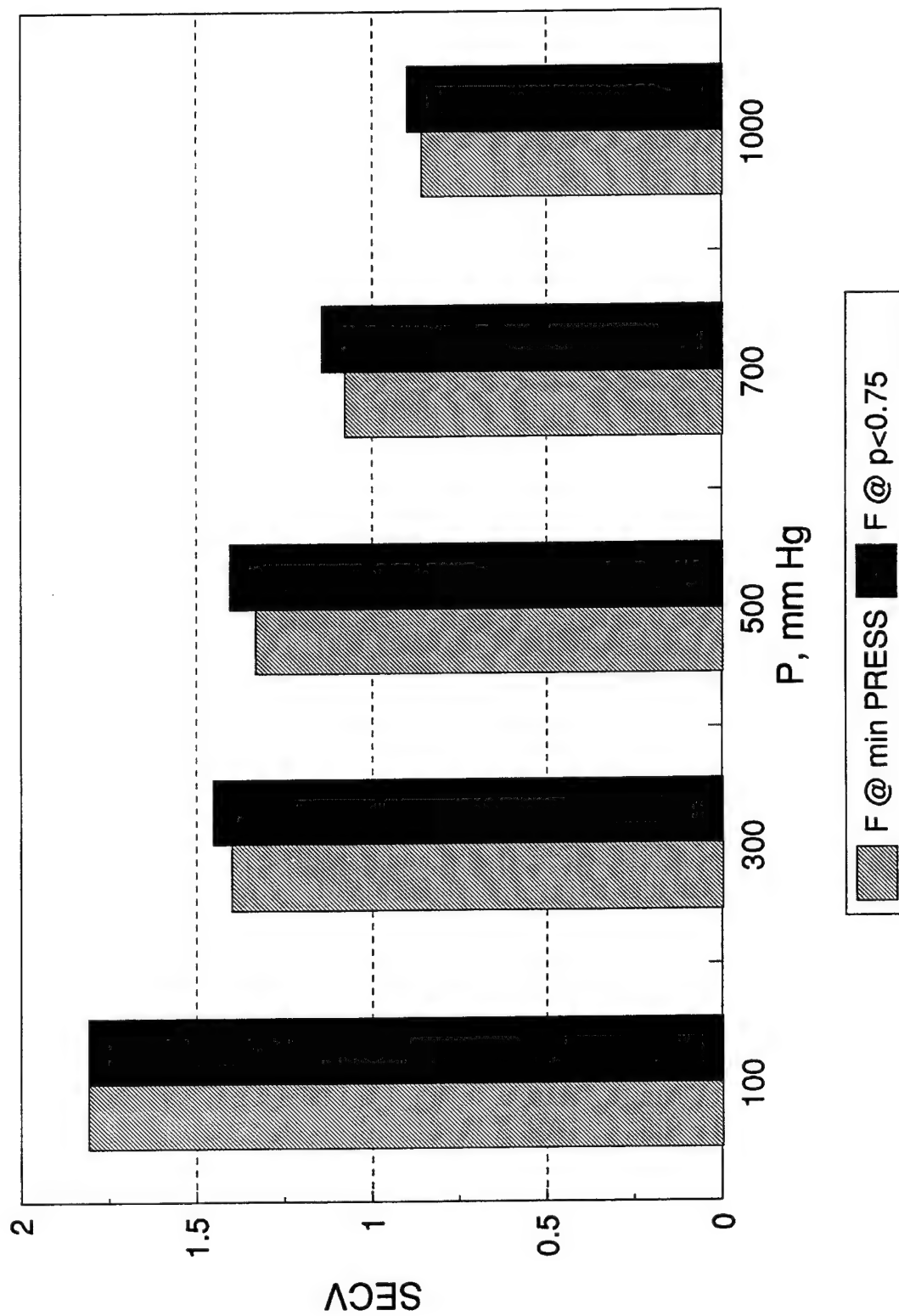


Figure B-17. Effect of cell pressure on SECV for "nitrogen" (pressure-based analysis)

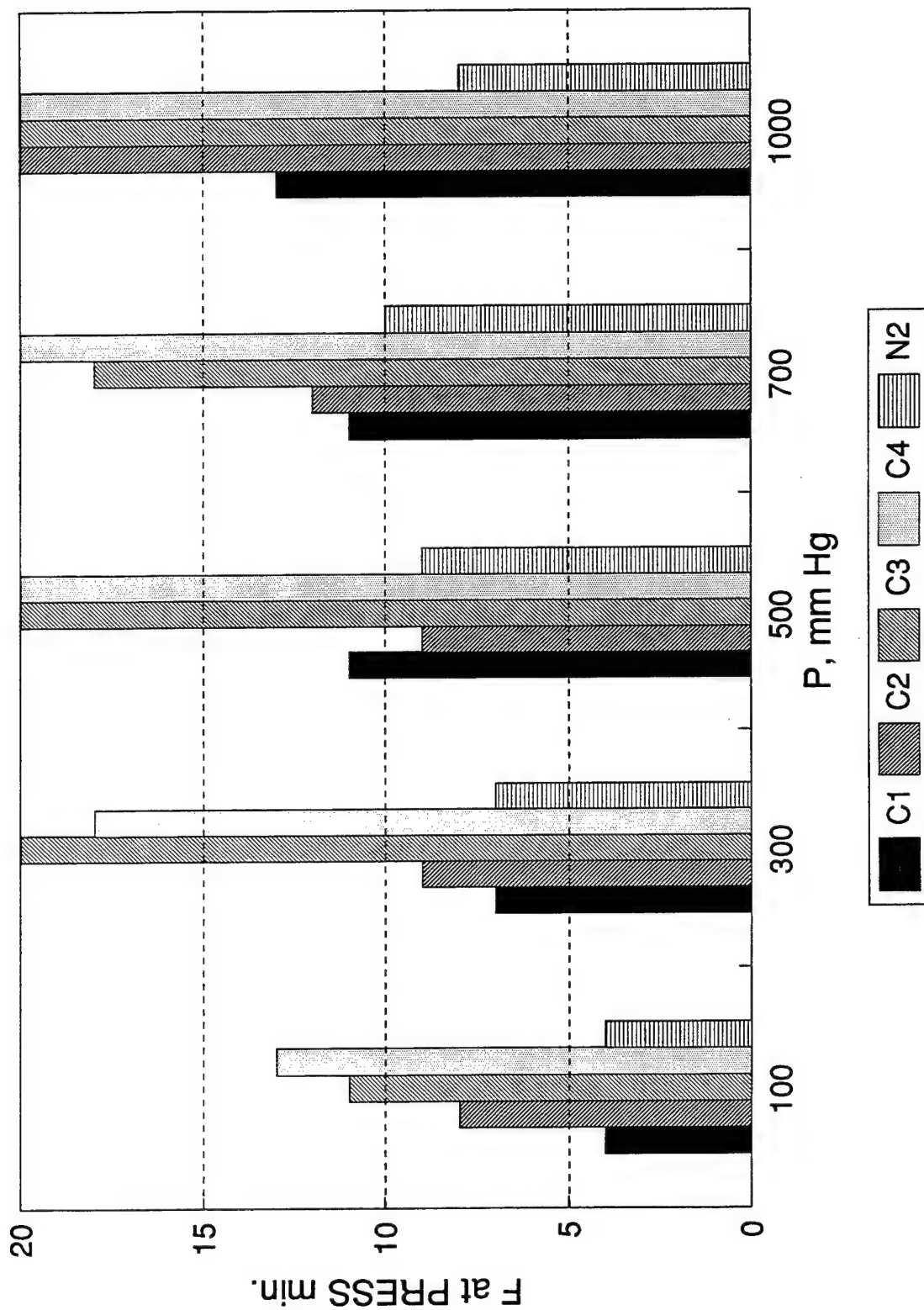


Figure B-18. Effect of cell pressure on the number of factors (F min. PRESS; pressure-based analysis)

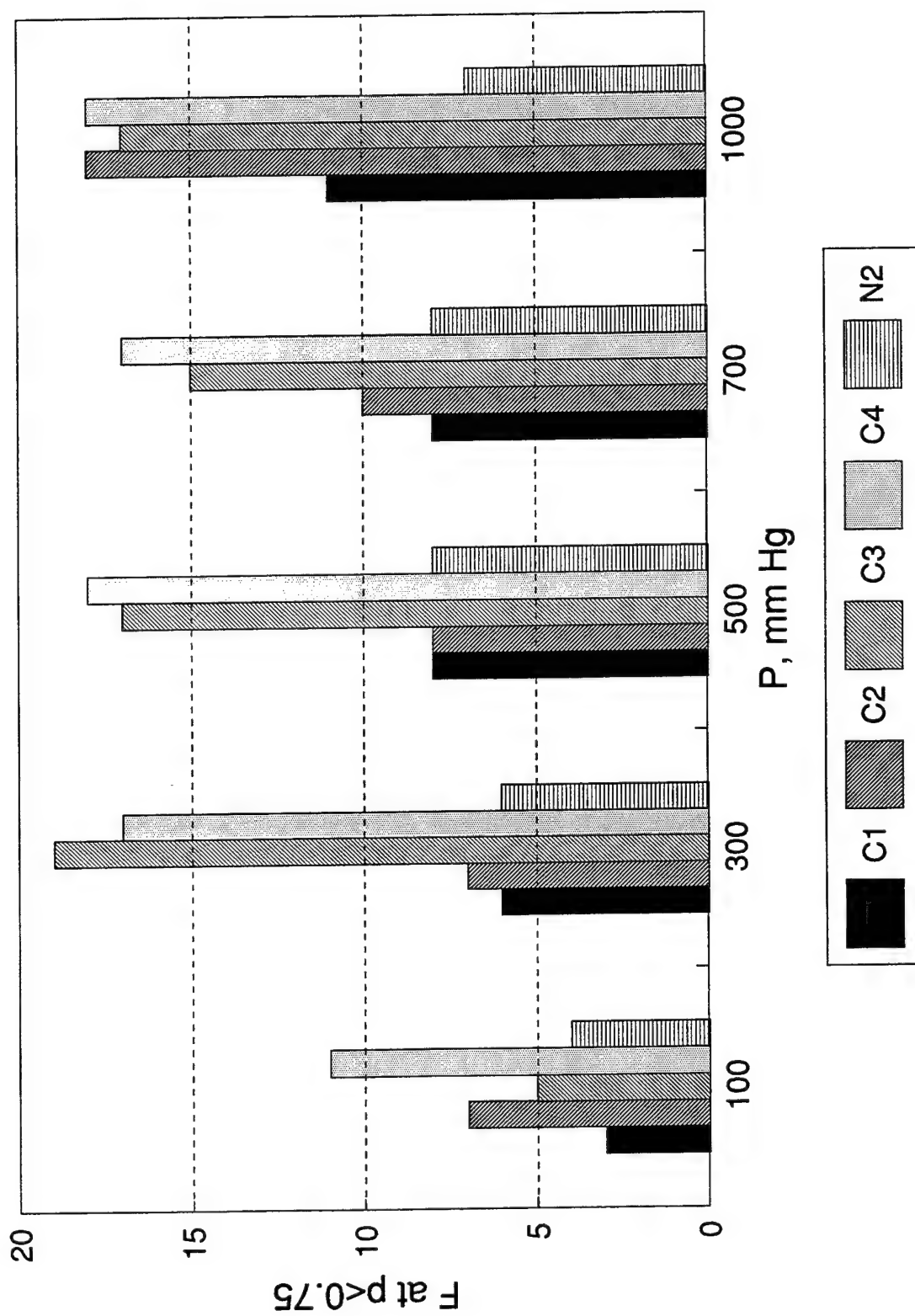


Figure B-19. Effect of cell pressure on the number of factors (F at $p < 0.75$; pressure-based analysis)

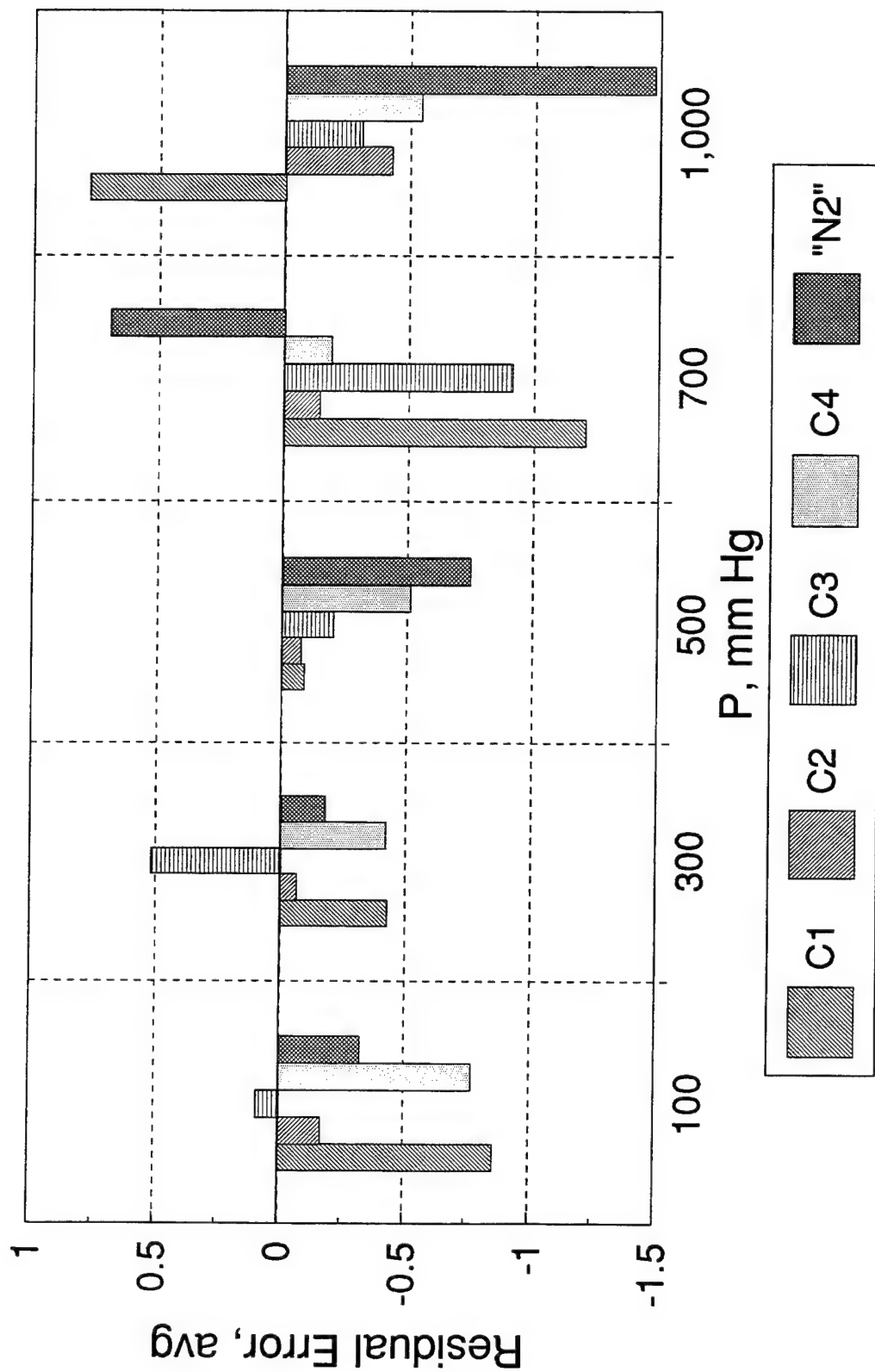


Figure B-20. Effect of cell pressure on the residual error in validation

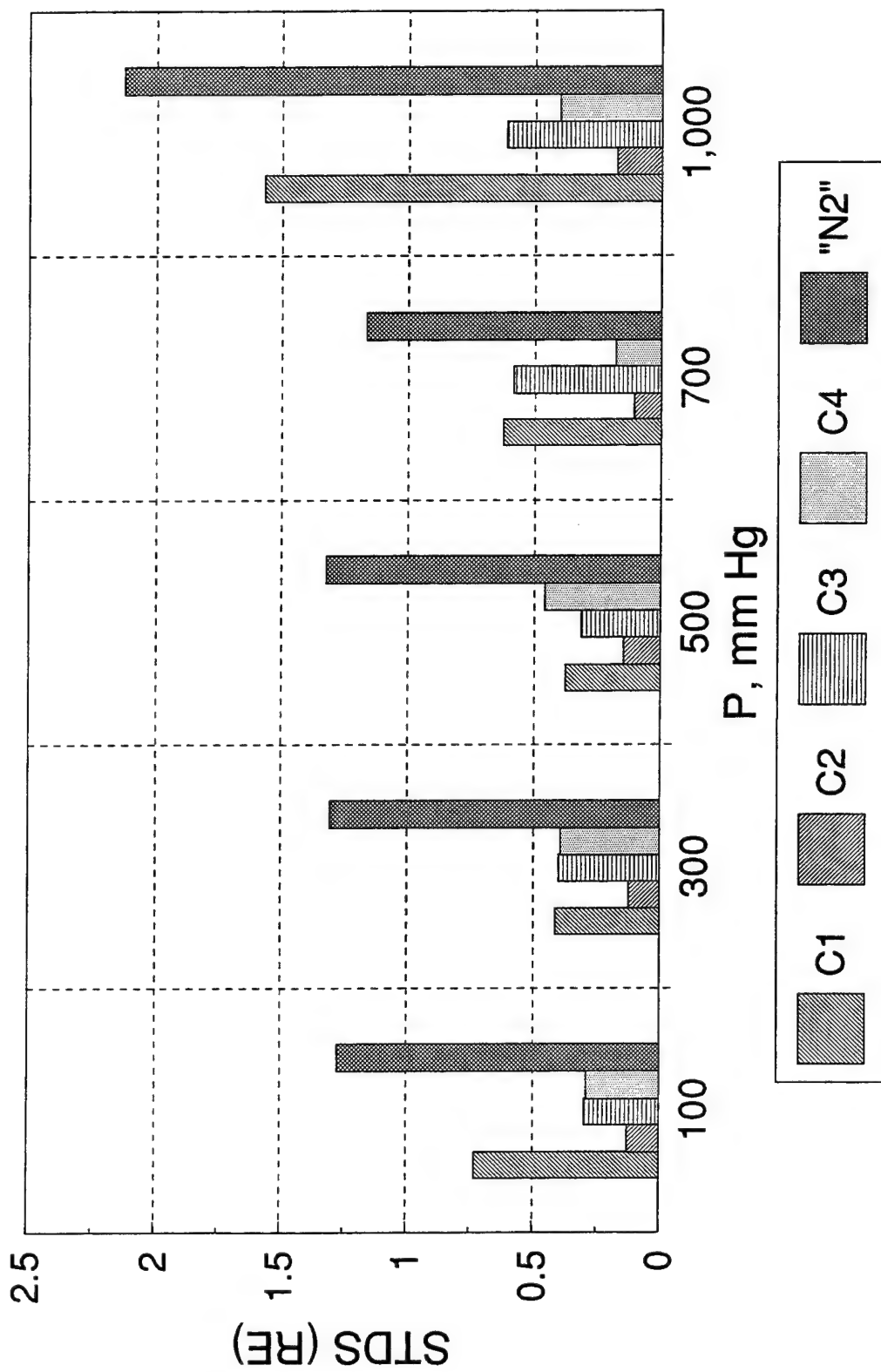


Figure B-21. Effect of cell pressure on the standard deviation of the residual error

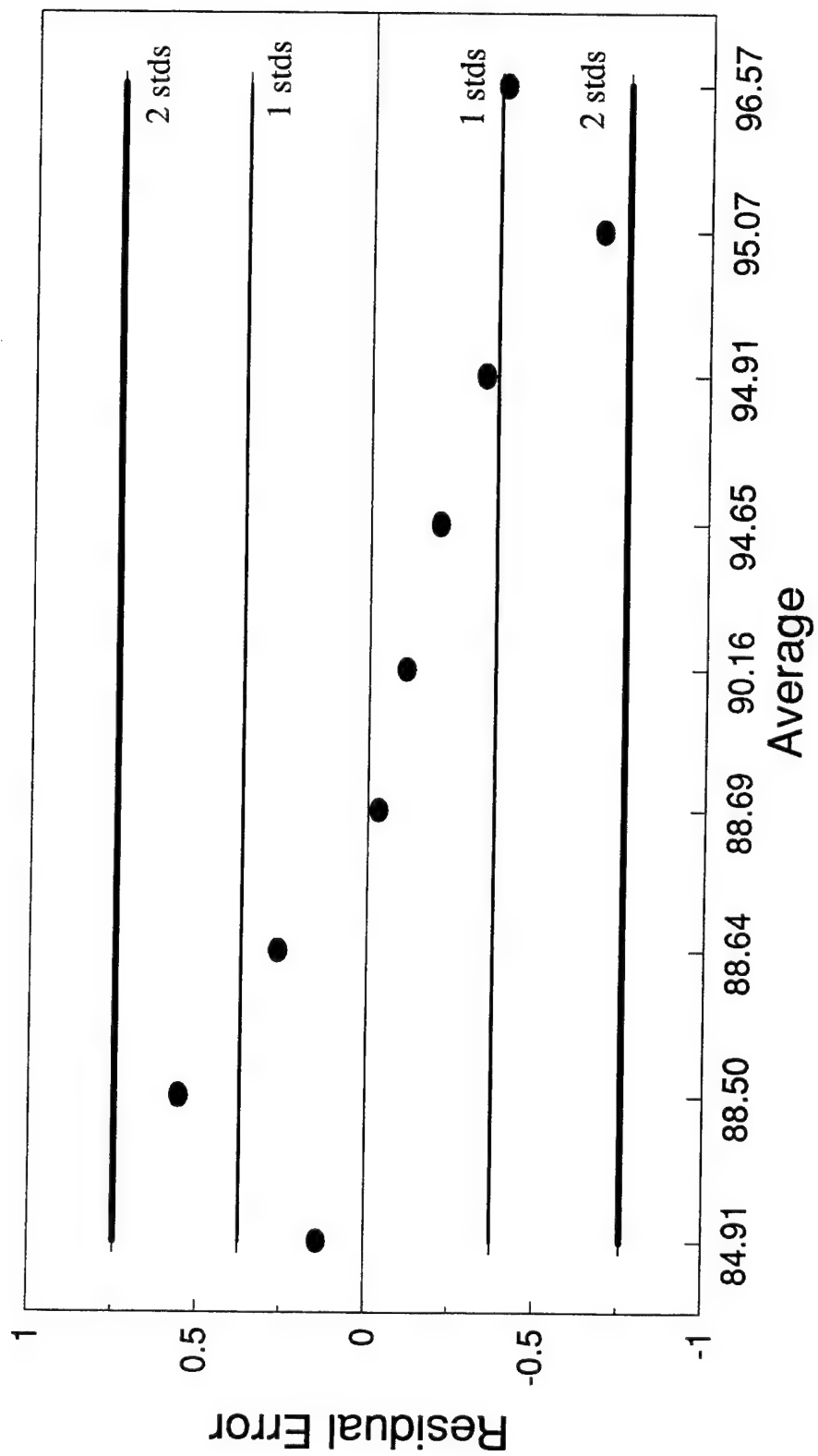


Figure B-22. Limits of agreement for methane validation at cell pressure of 500 mm Hg, abs

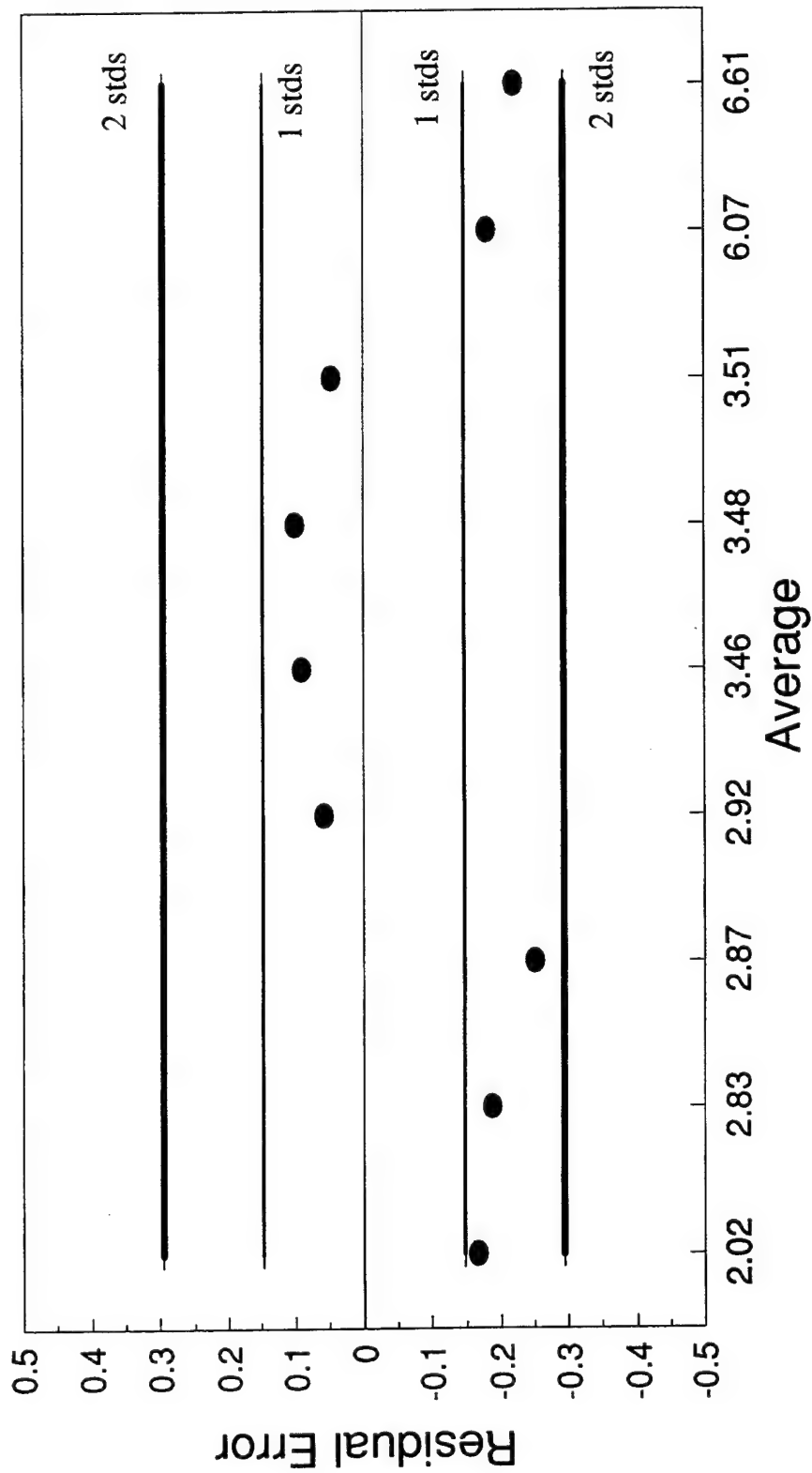


Figure B-23. Limits of agreement for ethane validation at cell pressure of 500 mm Hg. abs

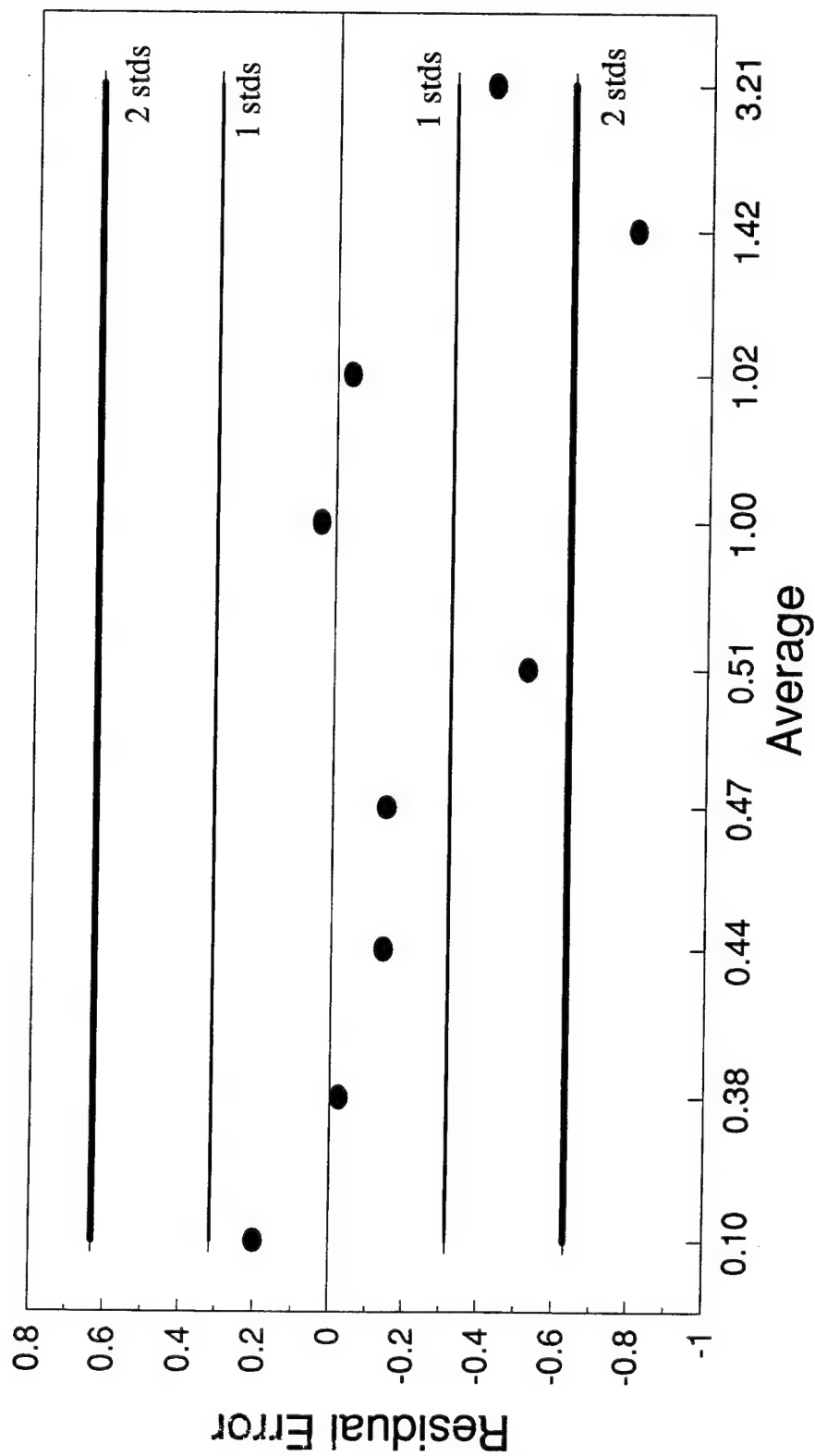


Figure B-24. Limits of agreement for propane validation at cell pressure of 500 mm Hg, abs

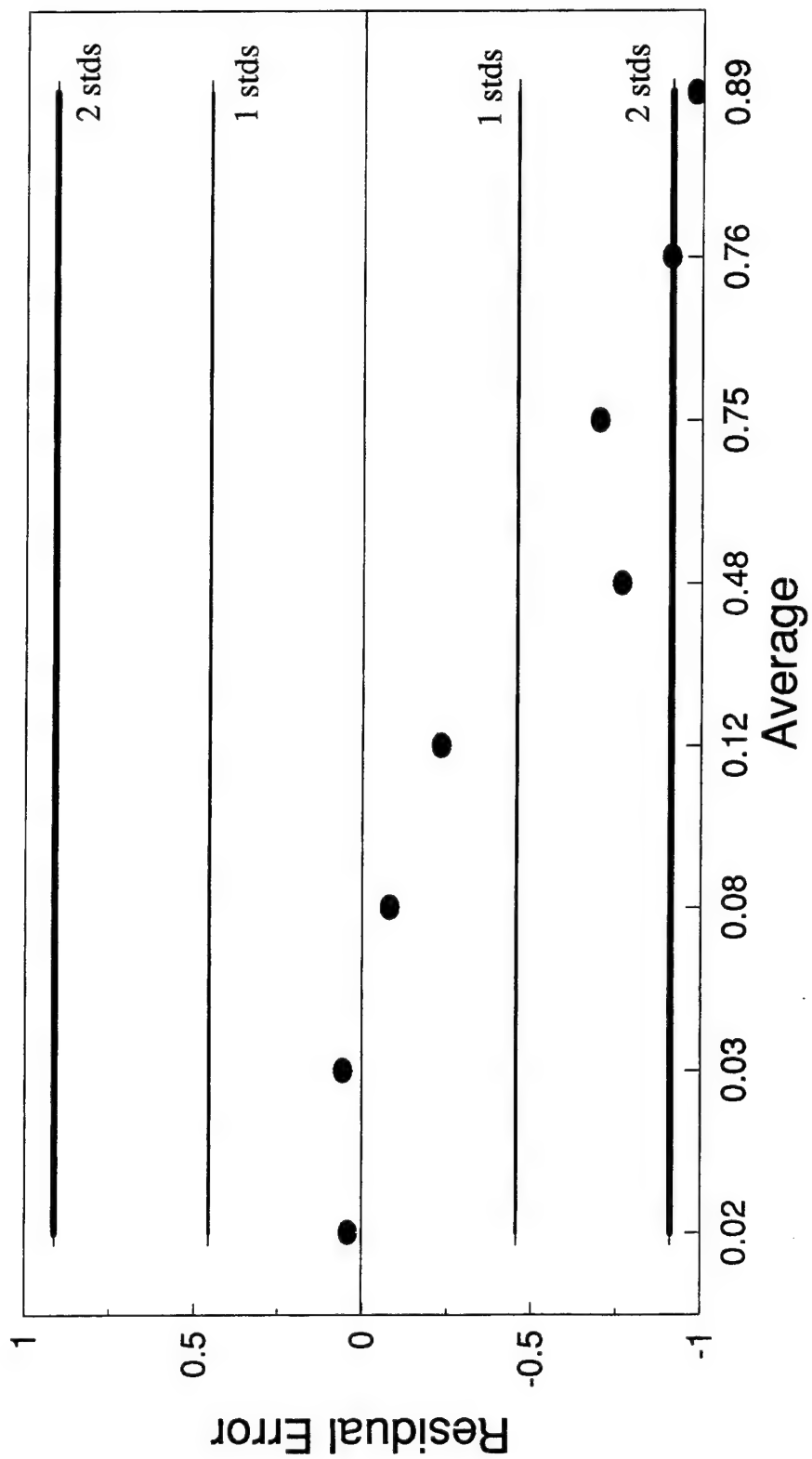


Figure B-25. Limits of agreement for butane validation at cell pressure of 500 mm Hg. abs

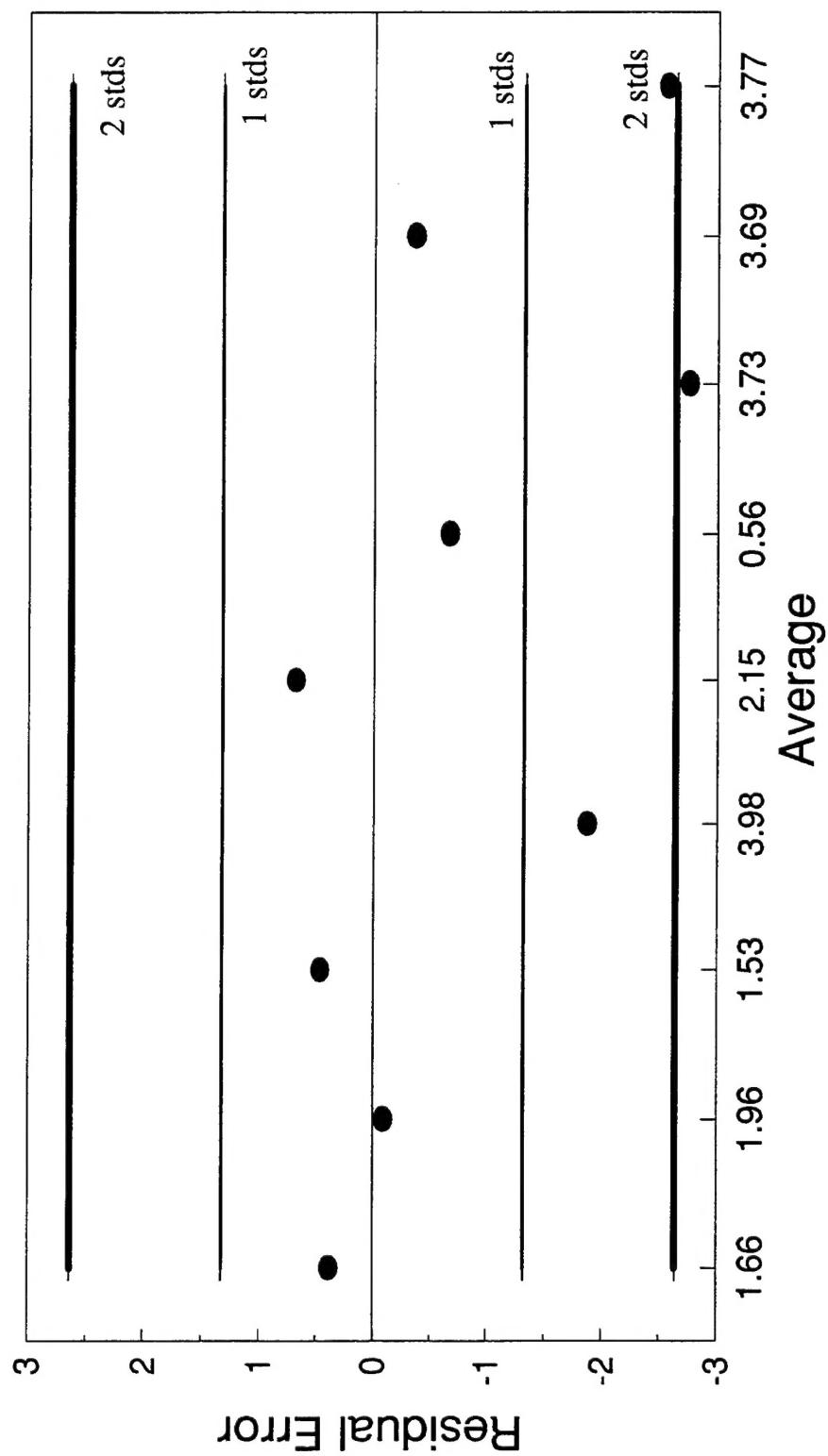


Figure B-26. Limits of agreement for "nitrogen" validation at cell pressure of 500 mm Hg. abs

DISTRIBUTION LIST

Department of Defense

| | | | |
|---|----|--|-------------|
| DEFENSE TECH INFO CTR ATTN: DTIC OCC 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218 | 12 | CDR DEFENSE FUEL SUPPLY CTR ATTN: DFSC A (S MURPHY) DFSC BP (R GRAY) DFSC BQ (L OPPENHEIM) 8725 JOHN J KINGMAN RD STE 2941 FT BELVOIR VA 22060-6222 | 1 1 1 |
| ODUSD ATTN: (L) MRM PETROLEUM STAFF ANALYST PENTAGON WASHINGTON DC 20301-8000 | 1 | DIR DEFENSE ADV RSCH PROJ AGENCY ATTN: ARPA/ASTO 3701 N FAIRFAX DR ARLINGTON VA 22203-1714 | 1 |
| ODUSD ATTN: (ES) CI 400 ARMY NAVY DR STE 206 ARLINGTON VA 22202 | 1 | | |

Department of the Army

| | | | |
|--|-----------------------|---|---------|
| HQDA ATTN: DALO TSE DALO SM 500 PENTAGON WASHINGTON DC 20310-0500 | 1 1 | MOBILITY TECH CTR BELVOIR ATTN: AMSTA RBF (M E LEPERA) AMSTA RBXA (R E TOBEY) 10115 GRIDLEY RD STE 128 FT BELVOIR VA 22060-5843 | 10 1 |
| SARDA ATTN: SARD TT PENTAGON WASHINGTON DC 20310-0103 | 1 | PROG MGR UNMANNED GROUND VEH ATTN: AMCPM UG REDSTONE ARSENAL AL 35898-8060 | 1 |
| CDR AMC ATTN: AMCRD IT 5001 EISENHOWER AVE ALEXANDRIA VA 22333-0001 | 1 | DIR ARMY RSCH LAB ATTN: AMSRL PB P 2800 POWDER MILL RD ADELPHIA MD 20783-1145 | 1 |
| CDR ARMY TACOM ATTN: AMSTA TR NAC MS 002 AMSTA TR R MS 202 AMSTA TR R MS 121 (C RAFFA) AMSTA TR R MS 158 (D HERRERA) USMC LNO WARREN MI 48397-5000 | 1 1 1 1 1 | VEHICLE PROPULSION DIR ATTN: AMSRL VP (MS 77 12) NASA LEWIS RSCH CTR 21000 BROOKPARK RD CLEVELAND OH 44135 | 1 |
| CDR AMSAA ATTN: AMXSY CM AMXSY L APG MD 21005-5071 | 1 1 | CDR ARO ATTN: AMXRO EN (D MANN) RSCH TRIANGLE PK NC 27709-2211 | 1 |
| CDR ARMY SOLDIER SPT CMD ATTN: SATNC US (J SIEGEL) SATNC UE NATICK MA 01760-5018 | 1 1 | CDR APC ATTN: SATPC L NEW CUMBERLAND PA 17070-5005 | 1 |

| | | | |
|----------------------------|---|--------------------------------|---|
| CDR ARMY TECOM | | CDR 49TH QM GROUP | |
| ATTN: AMSTE TA R | 1 | ATTN: AFFL GC | 1 |
| AMSTE TC D | 1 | FT LEE VA 23801-5119 | |
| AMSTE EQ | 1 | | |
| APG MD 21005-5006 | | CDR ARMY ORDN CTR | |
| | | ATTN: ATSL CD CS | 1 |
| PROJ MGR PETROL WATER LOG | | APG MD 21005 | |
| ATTN: AMCPM PWL | 1 | | |
| 4300 GOODFELLOW | | CDR ARMY SAFETY CTR | |
| ST LOUIS MO 63120-1798 | | ATTN: CSSC PMG | 1 |
| | | CSSC SPS | 1 |
| CDR | | FT RUCKER AL 36362-5363 | |
| ARMY BIOMED RSCH DEV LAB | | | |
| ATTN: SGRD UBZ A | 1 | CDR ARMY ABERDEEN TEST CTR | |
| FT DETRICK MD 21702-5010 | | ATTN: STEAC EN | 1 |
| | | STEAC LI | 1 |
| CDR FORSCOM | | STEAC AE | 1 |
| ATTN: AFLG TRS | 1 | STEAC AA | 1 |
| FT MCPHERSON GA 30330-6000 | | APG MD 21005-5059 | |
| | | | |
| CDR TRADOC | | CDR ARMY YPG | |
| ATTN: ATCD SL 5 | 1 | ATTN: STEYP MT TL M | 1 |
| INGALLS RD BLDG 163 | | YUMA AZ 85365-9130 | |
| FT MONROE VA 23651-5194 | | | |
| | | CDR ARMY CERL | |
| CDR ARMY QM SCHOOL | | ATTN: CECER EN | 1 |
| ATTN: ATSM PWD | 1 | P O BOX 9005 | |
| FT LEE VA 23001-5000 | | CHAMPAIGN IL 61826-9005 | |
| | | | |
| CDR ARMY TRANS SCHOOL | | PS MAGAZINE DIV | |
| ATTN: ATSP CD MS | 1 | ATTN: AMXLS PS | 1 |
| FT EUSTIS VA 23604-5000 | | DIR LOGSA | |
| | | REDSTONE ARSENAL AL 35898-7466 | |

Department of the Navy

| | | | |
|--------------------------|---|--------------------------|---|
| CDR | | CDR | 1 |
| NAVAL RSCH LABORATORY | | NAVAL PETROLEUM OFFICE | |
| ATTN: CODE 6181 | 1 | 8725 JOHN J KINGMAN RD | |
| WASHINGTON DC 20375-5342 | | STE 3719 | |
| | | FT BELVOIR VA 22060-6224 | |

Department of the Navy/U.S. Marine Corps

| | | | |
|--------------------------|---|------------------------|---|
| HQ USMC | | PROG MGR ENGR SYS | 1 |
| ATTN: LPP | 1 | MARINE CORPS SYS CMD | |
| WASHINGTON DC 20380-0001 | | 2033 BARNETT AVE | |
| | | QUANTICO VA 22134-5080 | |
| PROG MGR COMBAT SER SPT | 1 | | |
| MARINE CORPS SYS CMD | | CDR | |
| 2033 BARNETT AVE STE 315 | | 1ST MARINE DIV | 1 |
| QUANTICO VA 22134-5080 | | CAMP PENDLETON | |
| | | CA 92055-5702 | |
| CDR FMFPAC G4 | 1 | | |
| BOX 64118 | | | |
| CAMP H M SMITH | | | |
| HI 96861-4118 | | | |

TFLRF No. _____

Department of the Air Force

| | | | |
|---|---|--|---|
| HQ USAF/LGSF ATTN: FUELS POLICY 1030 AIR FORCE PENTAGON WASHINGTON DC 20330-1030 | 1 | SA ALC/SFT 1014 BILLY MITCHELL BLVD STE 1 KELLY AFB TX 78241-5603 | 1 |
| HQ USAF/LGTV ATTN: VEH EQUIP/FACILITY 1030 AIR FORCE PENTAGON WASHINGTON DC 20330-1030 | 1 | SA ALC/LDPG ATTN: D ELLIOTT 580 PERRIN BLDG 329 KELLY AFB TX 78241-6439 | 1 |
| AIR FORCE WRIGHT LAB ATTN: WL/POS 1790 LOOP RD N WRIGHT PATTERSON AFB OH 45433-7103 | 1 | WR ALC/LVRS 225 OCMULGEE CT ROBINS AFB GA 31098-1647 | 1 |
| AIR FORCE MEEP MGMT OFC OL ZC AFMC LSO/LOT PM 201 BISCAYNE DR BLDG 613 STE 2 ENGLIN AFB FL 32542-5303 | 1 | | |

Other Federal Agencies

| | | | |
|---|---|---|---|
| NASA LEWIS RESEARCH CENTER CLEVELAND OH 44135 | 1 | DOT FAA AWS 110 800 INDEPENDENCE AVE SW WASHINGTON DC 20590 | 1 |
| RAYMOND P. ANDERSON, PH.D., MANAGER FUELS & ENGINE TESTING BDM-OKLAHOMA, INC. 220 N. VIRGINIA BARTLESVILLE OK 74003 | 1 | EPA AIR POLLUTION CONTROL 2565 PLYMOUTH RD ANN ARBOR MI 48105 | 1 |